RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXVI NUMBER 4

October-December, 1953

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.

KOSMOS 60 RF KOSMOS 60 RF

KOSMOS 60 RF KOSMOS 60 RF

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

UNITED CARBON COMPANY, INC.

CHARLESTON 27, W. VA.

NEW YORK • AKRON • CHICAGO • BOSTON

CANADA: CANADIAN INDUSTRIES LIMITED

Rubber troubles? Feeling blue?
The **Philblacks*** *know just what to do!*

All Worn Out? Philblack E adds up to 42% more abrasion resistance to synthetic rubber tire treads.

Run Down? Philblack O and Philblack E give rubber remarkably long flex life.

Listless? Philblack I, the new ISAF black (Intermediate Super Abrasion Furnace) is prescribed for tread stocks. Gives unusually high abrasion at moderate added cost.

Jumpy Nerve? Fever? Philblack A removes nerve. Reduces heat build-up. Gives accurate moldings and smooth, fast tubings.

The Philblacks can help keep your business healthy. Consult our technical sales representative.

PHILLIPS CHEMICAL COMPANY

PHILBLACK SALES DIVISION

318 WATER STREET · AKRON 8, OHIO

PHILBLACK EXPORT SALES DIVISION

80 BROADWAY, NEW YORK 5, N. Y.

The Philblacks are manufactured at Borger, Texas.

Warehouses in Akron, Boston, Chicago and Trenton.

West Coast agent: Harwick Standard Chemical Company, Los Angeles.

Canadian agent: H. L. Blachford, Ltd., Montreal and Toronto.

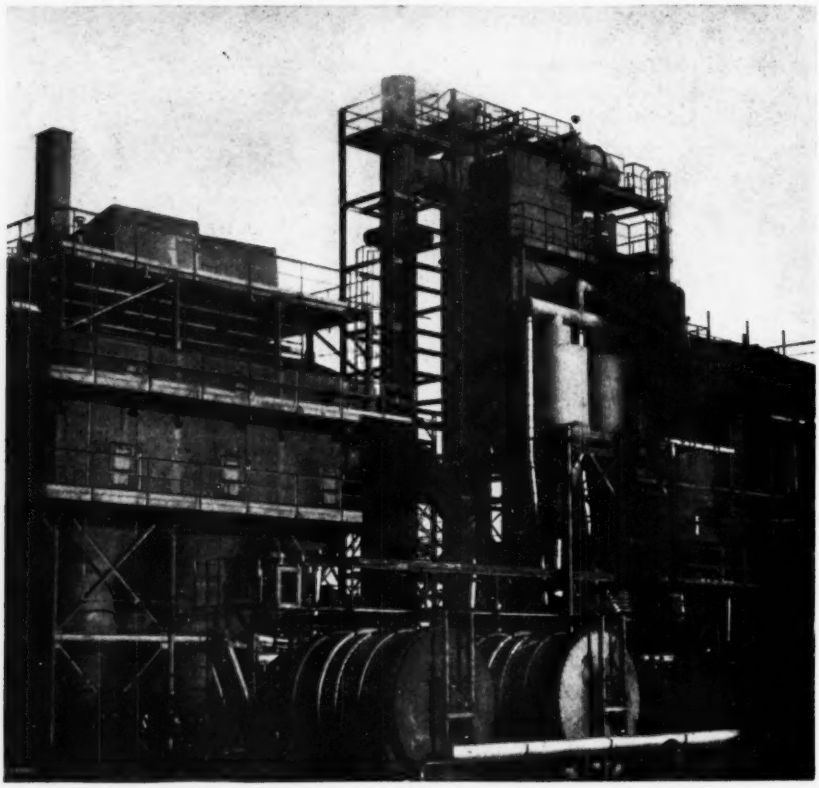
*A Trademark

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.

WITCO-CONTINENTAL'S

new facilities at Sunray—where CONTINEX® SRF, HMF and FEF Blacks are now in expanding production to meet your growing demands.

#3 unit at Sunray, Texas, showing bag filter, cyclone collector and pelletizing drums.



WITCO CHEMICAL COMPANY

CONTINENTAL CARBON COMPANY

260 Madison Avenue • New York 16, N. Y.

Akron • Amarillo • Los Angeles • Boston • Chicago • Houston
Cleveland • San Francisco • London and Manchester, England

Looking for better physicals?

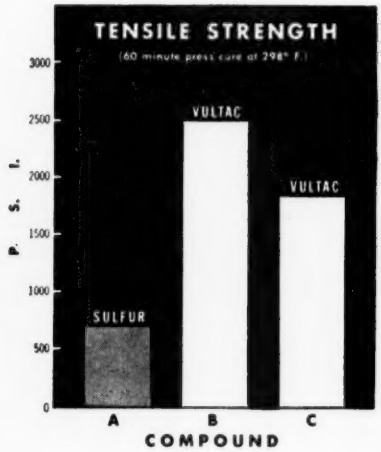
TRY VULTAC

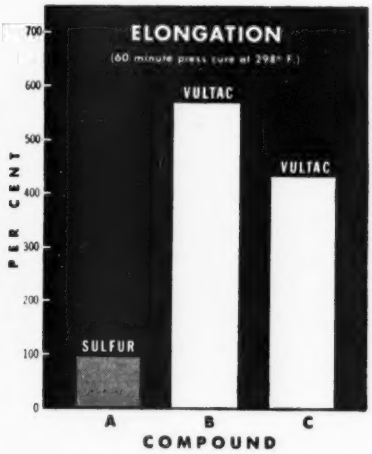
Here's what

VULTAC #3

does in a high zinc oxide, semi-hard compound

COMPOUND	A	B	C
Smoked Sheets	100	100	100
Zinc Oxide	70	70	70
Antioxidant	1	1	1
ETHYLAC	1	1	1
Sulfur	20	—	—
VULTAC #3	—	40	60
Total	192	212	232





The above is indicative of what the VULTACS do to the physical properties of a high zinc oxide compound when used as a total replacement for sulfur.

For samples and technical information write

SHARPLES TRADE MARK CHEMICALS

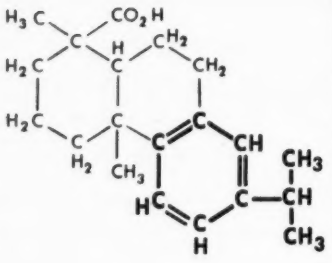
SHARPLES CHEMICALS INC.

A SUBSIDIARY OF THE PENNSYLVANIA SALT MANUFACTURING COMPANY

500 Fifth Ave., New York • 80 E. Jackson Blvd., Chicago • 106 S. Main St., Akron
Martin, Hoyt & Milne Inc., San Francisco • Los Angeles • Seattle • Portland
Shawinigan Chemicals, Ltd. • Montreal • Toronto
Airco Company International, New York

GALEX®

A superior tackifier and plasticizer for GR-S, NEOPRENE, NATURAL RUBBER and RECLAIM



FORMULA

"Galex" is a stable rosin acid that effectively tackifies and plasticizes GR-S, Neoprene, natural rubber and reclaim. Because of its chemical structure, principally dehydroabietic acid, "Galex" is unaffected by oxidative aging. It is compatible with various elastomers, resins and solvents.

"Galex" is widely used as a tackifier-plasticizer in hose, belting, mechanical goods and various friction stocks. It imparts strong surface tack which develops into excellent adhesion after cure. "Galex" also functions as a highly stable and compatible tackifier in rubber-base adhesives and cements.

"Galex" may be the tackifier-plasticizer you need to build maximum quality into *your* compound. Its superior tack, excellent aging resistance and high compatibility warrant your investigation. Write for technical information and samples.

Thiokol® Chemical Corporation

784 NORTH CLINTON AVENUE • TRENTON 7, NEW JERSEY

In Canada: Naugatuck Chemicals Division, Dominion Rubber Company, Elmira, Ontario

QUALITY PRODUCTS
worth knowing and using

PLIOVIC

PLIOVIC G80V – General-purpose, medium to high molecular weight polyvinyl chloride resin. Designed for low temperature processing (310-320F.) Has excellent resistance to heat and light. Handles easily. Processes rapidly. Gives films of exceptional clarity and good general properties.

PLIOVIC G90V–General-purpose, medium to high molecular weight polyvinyl chloride resin. Similar to PLIOVIC G80V, but designed for average to high temperature processing. Finished products have generally higher physical properties.

PLIOVIC AO – High molecular weight copolymer resin of high vinyl chloride content. Particularly suited to use in organosols, plastisols and plastigels.

PLIOLITE S-6B

High styrene copolymer resin for reinforcing rubber. Noted for finer, faster dispersions and outstanding properties imparted to rubber. Greatly increases hardness, stiffness, flex-life and tear strength. Exhibits low gravity, light color, excellent chemical resistance and electrical properties.

CHEMIGUM

Oil-resistant rubbers of medium to high acrylonitrile content. Unusually easy to process. Exhibit optimum physical properties and excellent resistance to oils, greases, solvents and chemicals. Permit the meeting of virtually any specification calling for oil-resistant rubber.

Wing-Stay S

Liquid, nonstaining antioxidant for natural and synthetic rubbers. Displays outstanding resistance to heat, sunlight and extraction by water. Offers best available balance of permanence, protection, low cost and nonstaining, non-discoloring properties Available in several GR-S rubbers or in bulk.

CHEMICAL GOODYEAR DIVISION

GET MORE OUT OF YOUR PLANT—
PUT THESE PRODUCTS IN!
For full details and samples, write to:
Goodyear, Chemical Division,
Akron 16, Ohio

Use Proved Products – CHEMIGUM · PLIOBOND · PLIOLITE · PLIOVIC · WING CHEMICALS – The Finest Chemicals for Industry

Chemigum, Pliobond, Pliolite, Pliovic, Wing-Stay–T. M.'s The Goodyear Tire & Rubber Company, Akron, Ohio

THE HISTORY OF THE RUBBER INDUSTRY—Number 4

how long did it take to get from here to here?

Answer: Four Years

In 1916, solid rubber truck tires outnumbered pneumatics 60 to 1, but World War I demonstrated the superiority of pneumatics. As old trucks wore out after the 1920 depression—four years later—and business picked up, the solids began disappearing. By 1941, only one truck tire in 10,000 was a solid.

Many Monsanto products have aided the progress of the Rubber Industry.

FLECTOL H, for example, is a Monsanto antioxidant for natural and synthetic rubber. Flectol H is an excellent protector against heat deterioration and normal aging. It causes less discoloration than most other full-power antioxidants.

Write for booklet "Monsanto Chemicals for the Rubber Industry." Address: MONSANTO CHEMICAL COMPANY, Rubber Chemical Sales, 920 Brown Street, Akron 11, Ohio.

6

Monsanto Chemicals For the Rubber Industry

ANTIOXIDANTS
Flectol* H
Santoflex* B
Santoflex BX
Santoflex 35
Santoflex AW
Santowhite* Crystals
Santowhite MK
Santowhite L

ALDEHYDE AMINE ACCELERATORS
A-32
A-100

MERCAPTO ACCELERATORS
Santocure*
El-Sixty*
Mertax (Purified Thiotax)
Thiotax (2-Mercapto benzothiazole)
Thiofide* (2,2' dithio-bis benzothiazole)

GUANIDINE ACCELERATORS
Diphenylguanidine (D.P.G.)
Guantal*

ULTRA ACCELERATORS FOR LATEX, ETC.
R-2 Crystals
RZ-50
RZ-50-B
Pip-Pip
Thiurad* (Tetramethylthiuram disulfide)
Ethyl Thiurad (Tetraethylthiuram disulfide)
Mono Thiurad (Tetramethylthiuram monosulfide)
Methasan* (Zinc salt of dimethyl dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl dithiocarbamic acid)

WETTING AGENTS AND DETERGENTS
Aresksp* 50
Aresklene* 375
Santomerse* S
Santomerse D

SPECIAL MATERIALS
Thiocarbanilide ("A-1")
Santovar*-A
Santovar-O
Sulfasan R
Insoluble Sulfur "60"

COLORS

REODORANTS

**Reg. U.S. Pat. Off.*

MONSANTO
CHEMICALS—PLASTICS

SERVING INDUSTRY... WHICH SERVES MANKIND

...rough going

The going is smooth for you now, but eventually it will get rough because of the ever-decreasing production of channel black. It might be well to consider the Sid Richardson Carbon Co. as your future supplier.

The rapid diverson of natural gas from plants to pipe lines foretells this eventual shortage of channel black. Our own extensive supplies of natural gas and other resources, plus the world's largest channel black plant, enable the Sid Richardson Carbon Co. to assure you a *continuing supply* of top-quality, uniform, economical-to-use **TEXAS "E"** and **TEXAS "M"** channel blacks.

TEXAS
CHANNEL BLACKS

Sid Richardson
CARBON CO.
FORT WORTH, TEXAS

GENERAL SALES OFFICES
EVANS SAVINGS AND LOAN BUILDING
AKRON 8, OHIO

Look at...

HYDROCARBON

PANAREZ

RESINS

AS A QUALITY ECONOMICAL RESIN IN RUBBER COMPOUNDING

PANAREZ hydrocarbon resins are effective and inexpensive for rubber compounding. They have low specific gravity · Low odor · Show no effect on cure · There is a marked improvement in processing · Longer flex life · Greater abrasion resistance · Better color stability · Electrical characteristics are excellent.

Prompt shipments made in carload or single drum quantities. Write for samples.

	Color Gardner	Softening Point, °F	Specific Gravity	Acid Number
PANAREZ 3-210	9	200-220	1.049	0-1
PANAREZ 6-210	11	200-220	1.106	0-1
PANAREZ 12-210	16	200-220	1.054	0-1

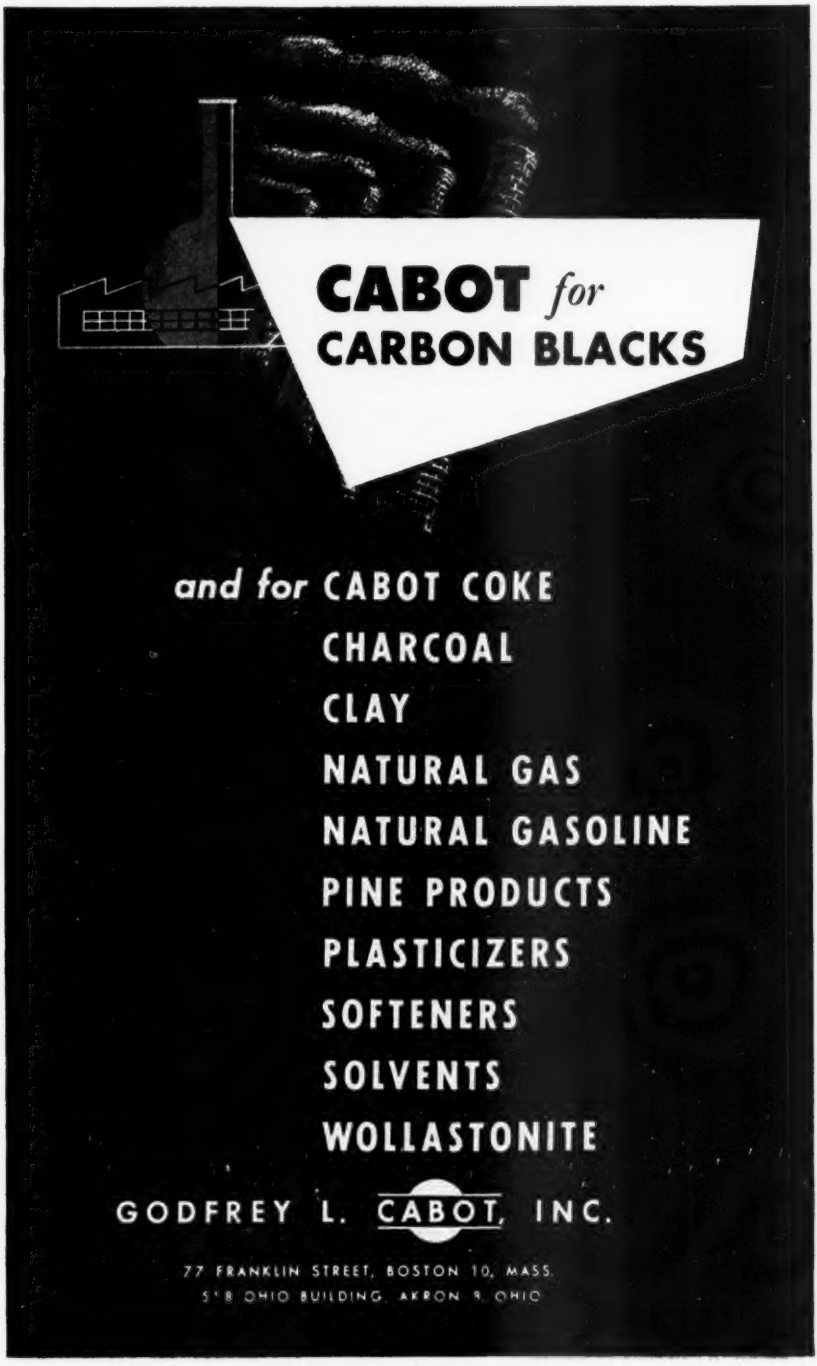
PAN AMERICAN CHEMICALS

PAN AMERICAN *Chemicals*

DIVISION

Pan American Refining Corp.

122 EAST 42ND STREET · NEW YORK 17, N. Y.


CABOT for
CARBON BLACKS
and for CABOT COKE
CHARCOAL
CLAY
NATURAL GAS
NATURAL GASOLINE
PINE PRODUCTS
PLASTICIZERS
SOFTENERS
SOLVENTS
WOLLASTONITE
GODFREY L. CABOT, INC.
77 FRANKLIN STREET, BOSTON 10, MASS.
518 OHIO BUILDING, AKRON 8, OHIO

Performance You Can Rely On!

NEOPRENE

THERE'S A TYPE TO MEET YOUR EXACT REQUIREMENTS

DRY NEOPRENES

GENERAL-PURPOSE TYPES

TYPE GN. Suitable for use in non-staining and light-colored compounds.

TYPE GN-A. Contains a stabilizer that results in improved storage stability; will stain and discolor.

TYPE GRT. Recommended for compounds requiring improved tack retention and maximum resistance to crystallization.

TYPE W. Possesses outstanding storage stability and excellent processing characteristics. Produces vulcanizates having light color, good heat resistance and low permanent set.

TYPE WRT. For use wherever the properties of Type W are desired plus maximum resistance to crystallization.

SPECIAL-PURPOSE TYPES

TYPE AC. Especially developed for quick-setting adhesive cements. Superior in stability and color.

TYPE KNR. Especially developed for high-solids cements, putties and doughs.

TYPE Q. For maximum resistance to oils, chemicals and solvents, particularly EP lubricants, refrigerants and nonflammable hydraulic fluids.

TYPE S. Especially developed for crepe soles. Also used as a stiffening agent for processing other neoprenes.

NEOPRENE LATICES

TYPE 571 (Solids 50% ± 1%)—General-purpose type for most applications.

TYPE 572 (Solids 50% ± 1%)—Fast-setting, high wet-strength type for adhesives.

TYPE 601A (Solids 59% ± 1%)—For dipped and coated goods and for foam. Improved resistance to crystallization.

TYPE 735 (Solids 35% ± 1%)—A sol type latex. Specially suited for paper making. Used with other latices to improve wet gel strength and extensibility.

TYPE 842A (Solids 50% ± 1%)—General-purpose, fast-curing type; vulcanizates have improved resistance to crystallization. Recommended for dipping, saturation, and as a binder for fibers.

NEOPRENE RESISTS:
Oxidation • Heat • Sunlight • Ozone • Oils • Grease • Chemicals • Aging • Abrasion • Flame • Flex-Cracking.

JUST PUBLISHED—*"The Neoprenes." Here's a 250-page book on the principles of compounding and processing all types of dry neoprene. It's free for the asking. Your Du Pont representative will be glad to secure a copy for you. Just write or phone the nearest Rubber Chemicals district office.*

DISTRICT OFFICES:

Akron 8, Ohio, 40 E. Buchtel Ave. . . . . HEmlock 3161
Atlanta, Ga., 1261 Spring St., N.W. . . . . EMerson 5391
Boston 5, Mass., 140 Federal St. . . . . HAncock 6-1711
Chicago 3, Ill., 7 S. Dearborn St. . . . . ANdover 3-7000
Houston, Texas, 4141 Dennis St. . . . . ATwood 4566
Los Angeles 58, Cal., 2930 E. 44th St. . . . . LOgan 5-6464
New York 13, N. Y., 40 Worth St. . . . . COrtlandt 7-3966
Wilmington 98, Del., 1007 Market St. . . . . Wilm. 4-5121

DU PONT RUBBER CHEMICALS

DU PONT

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

chemicals for the rubber industry

ACCELERATORS

Thiazole

- MBT (Mercaptobenzothiazole)
- MBT-XXX (Specially Refined—Odorless)
- MBTS (Benzothiazyldisulfide)
- NOBS* No. 1 Accelerator

Guanidine

- DPG (Diphenylguanidine)
- DOTG (Diorthotolylguanidine)
- Accelerator 49

ANTIOXIDANT

Antioxidant 2246*
(Non-staining, non-discoloring type)

PEPTIZER

Pepton® 22 Plasticizer

RETARDER

Calco Retarder P.D.

STIFFENING AGENT

Calco S.A.

SULFUR

Rubber Makers' Grade

*Trade-mark

AMERICAN *Cyanamid* COMPANY Calco®

CALCO CHEMICAL DIVISION
INTERMEDIATE & RUBBER CHEMICALS DEPARTMENT
BOUND BROOK, NEW JERSEY, U.S.A.

SALES REPRESENTATIVES AND WAREHOUSE STOCKS: Akron Chemical Company, Akron, Ohio • Ernest Jacoby and Company, Boston, Mass. • Herron & Meyer of Chicago, Chicago, Ill. • H. M. Royal, Inc., Los Angeles, Calif. • H. M. Royal, Inc., Trenton, N. J. • In Canada: St. Lawrence Chemical Company, Ltd., Montreal and Toronto

Start the New Year Right

BY CALLING ON **NAUGATUCK** CHEMICAL

TO PROCESS—ACCELERATE—PROTECT
YOUR RUBBER PRODUCTS

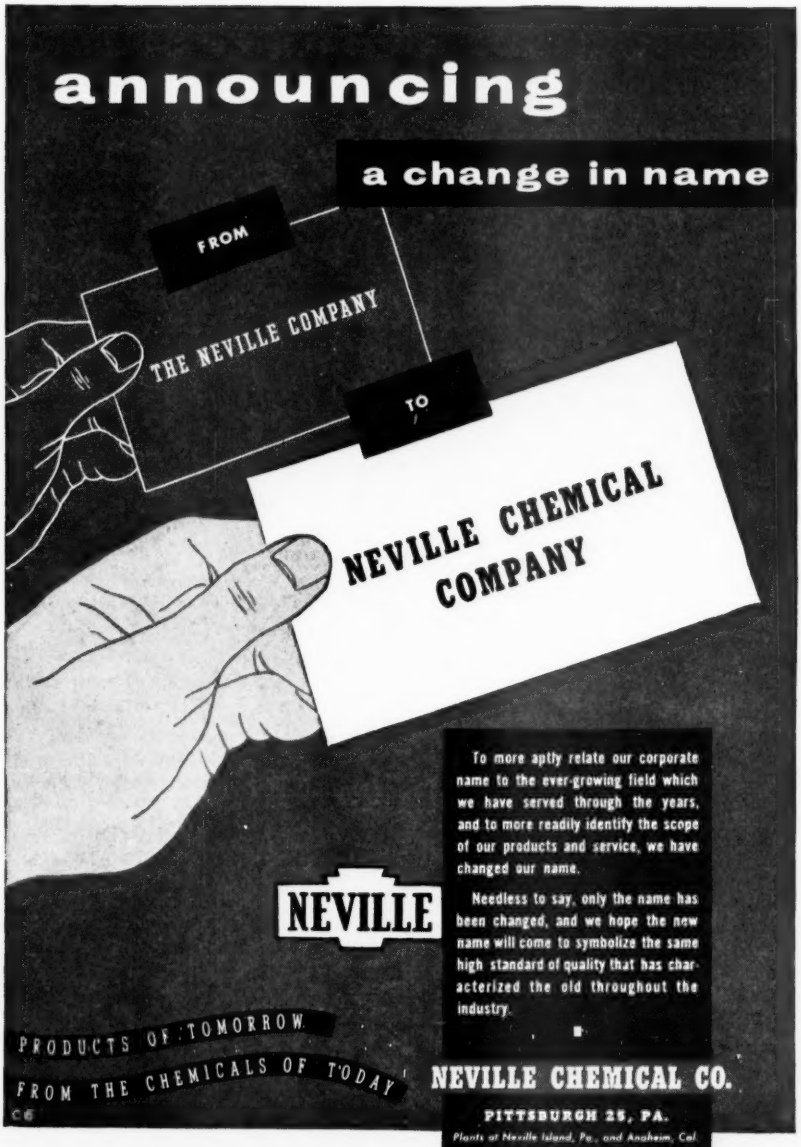
PROCESSING LAUREX, activator · BWH-1, plasticizer · Kralac A, high styrene resin · ESEN, retarder

ACCELERATING THIAZOLES—MBT • MBTS • OXAF
THIURAMS—MONEX • TUEX • PENTEX
DITHIOCARBAMATES—ARAZATE • BUTAZATE • ETHAZATE • METHAZATE
ALDEHYDE AMINES—BEUTENE • HEPTEEN BASE • TRIMENE BASE
XANTHATES—CPB • ZBX
SPECIAL ACTIVATORS—DBA • GMF • VULKLOR • DIBENZO GMF

PROTECTING ANTIOXIDANTS
AMINOX • ARANOX • BLE-25 • FLEXAMINE • BETANOX SPECIAL

NEW! *CELOGEN—Blowing Agent For Rubber and Plastics*

Naugatuck Chemical
Division of United States Rubber Company
NAUGATUCK CONNECTICUT


announcing
a change in name
FROM
THE NEVILLE COMPANY
TO
NEVILLE CHEMICAL COMPANY
To more aptly relate our corporate name to the ever-growing field which we have served through the years, and to more readily identify the scope of our products and service, we have changed our name.
Needless to say, only the name has been changed, and we hope the new name will come to symbolize the same high standard of quality that has characterized the old throughout the industry.
NEVILLE
PRODUCTS OF TOMORROW
FROM THE CHEMICALS OF TODAY
NEVILLE CHEMICAL CO.
PITTSBURGH 25, PA.
Plants at Neville Island, Pa., and Anaheim, Cal.

ADVERTISE *in*

RUBBER CHEMISTRY AND TECHNOLOGY

KEEP YOUR NAME AND YOUR PRODUCTS CONSTANTLY BEFORE THE RUBBER TECHNOLOGIST

Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, care of E. I. du Pont de Nemours & Company, 40 East Buchtel Ave. at S. High St., Akron 8, Ohio.

Styrene Monomer Starts at Koppers

● Styrene Monomer, which traces its chemical origin to coal, is a basic product at Koppers, for Koppers has been a leader in the coal carbonization industry for many years. Koppers has its own raw materials for Styrene Monomer, thereby assuring a continuity of supply.

Styrene Monomer has found extensive application in the manufacture of polystyrene plastics and synthetic rubbers, including GR-S Rubber for tires and other rubber-styrene copolymers for most commerical rubber applications including hose, shoe soles, floor tiles, and rubber mechanical goods.

It is also used in the manufacture of styrene resins for coating and impregnating porous and fibrous materials, and in the manufacture of polyester laminating resins, styrenated drying oils and styrenated alkyds for paints, enamels and varnishes.

When looking for a dependable source of supply for vital industrial chemicals, it's good business to look to the leaders. Koppers, one of the country's major manufacturers of Styrene Monomer, is prepared to give you the quickest, best service possible, because its producing plant is *centrally* located. Styrene is supplied in tank-car, tank-truck, and 55-gallon drum quantities.

KOPPERS COMPANY, INC.

Chemical Division, Dept. RCT-123, Pittsburgh 19, Pennsylvania

KOPPERS®

Koppers Chemicals

SALES OFFICES: NEW YORK · BOSTON · PHILADELPHIA · ATLANTA
CHICAGO · DETROIT · LOS ANGELES

CIRCOSOL-2XH IS VERSATILE

. . . a process aid

Circosol-2XH has extremely wide application because of its relatively low staining properties, and because it assures the most favorable physical characteristics in the finished vulcanizates.

. . . an elasticator

Circosol-2XH greatly improves the rebound properties of GR-S vulcanizates.

. . . a polymer extender

Circosol-2XH assures uniformity, with a minimum of down-grading.

Because of its versatility, Circosol-2XH is ideal for use in such diversified products as light colored footwear, hospital sheeting, white seals and gaskets, white side-wall tires, sponge rubbers and toys.

Let us tell you the complete story of Circosol-2XH. Write for technical bulletin or have our representative call. SUN OIL COMPANY, Phila. 3, Pa., Dept. RC-10.

INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY

SUNOCO®

PHILADELPHIA 3, PA. • SUN OIL COMPANY LTD., TORONTO & MONTREAL

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXVI NUMBER 4

October-December, 1953

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

CARBON BLACKS

for **RUBBER COMPOUNDING**

SAF (Super Abrasion Furnace)
STATEX®-125

HAF (High Abrasion Furnace)
STATEX-R

MPC (Medium Processing Channel)
STANDARD MICRONEX®

EPC (Easy Processing Channel)
MICRONEX W-6

FF (Fine Furnace)
STATEX-B

FEF (Fast Extruding Furnace)
STATEX-M

HMF (High Modulus Furnace)
STATEX-93

SRF (Semi-Reinforcing Furnace)
FURNEX®

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON CO. • **BINNEY & SMITH CO.**
MANUFACTURER DISTRIBUTOR

500 TONS OF SMOKE A DAY

RUBBER CHEMISTRY AND TECHNOLOGY

Published Quarterly under the Auspices of the Division of Rubber Chemistry
of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor ..... C. C. DAVIS
Advertising Manager ..... E. H. KRISMANN
Secretary ..... C. R. HAYNES
Treasurer ..... A. W. OAKLEAF

Vol. XXVI **October-December, 1953** **No. 4**

CONTENTS

General Section PAGE

Officers iii
Spring Meeting of the Division of Rubber Chemistry, Los Angeles, Calif., March 18 and 19, 1953 v
Spring Meeting of the Division of Rubber Chemistry, Boston, Mass., May 27 to 29, 1953 vi
Fall Meeting of the Division of Rubber Chemistry, Chicago, Illinois, September 9 to 11, 1953 viii
New Books and Other Publications x

Papers

Cross-Linking in Natural-Rubber Vulcanizates. H. E. ADAMS AND B. L. JOHNSON 741
Thermal Decomposition of Vulcanized Structures of Deformed Vulcanizates Containing Various Accelerators. B. DOGADKIN AND Z. TARASOVA 759
The Viscometric Detection of Branching in Polymers. I. Branching in GR-S as a Function of Conversion. L. H. CRAGG AND A. T. BROWN 764
Viscometric Detection of Branching in Polymers. II. Branching in Poly (Buta-Diene-Co-Styrene) as a Function of Polymerization Temperature. L. H. CRAGG AND G. R. H. FERN 775
Structural Changes in Rubber Caused by the Action of Molecular Oxygen. V. Destructive Solution of Vulcanized Synthetic Rubbers. Z. TARASOVA AND B. DOGADKIN 787
Degradation of Natural Rubber in Solution in Vacuo. W. F. WATSON 798
Structure and Properties of Loaded Rubber Mixtures. IX. Modification of Carbon Structures by Repeated Deformations. K. PECHKOVSKAYA, TS. MIL'MAN, AND B. DOGADKIN 810
Structure and Properties of Loaded Rubber Mixtures. X. Alteration of Carbon Black Structures by Heat Treatment. B. A. DOGADKIN, K. PECHKOVSKAYA, AND TS. MIL'MAN 821
The Effect of Comonomer on the Microstructure of Butadiene Copolymers. FREDERICK C. FOSTER AND JOHN L. BINDER 832
Self-Inhibition in the Oxidation of Butadiene-Acrylonitrile Rubbers. A. S. KUZMINSKIĬ AND E. B. POPOVA 840

Acrylic Elastomers. Preparation and Properties of Vulcanizable Acrylic Ester-Acrylonitrile Copolymers. E. M. Filachione, T. J. Fitzpatrick, C. E. Rehberg, C. F. Woodward, W. E. Palm, and J. E. Hansen 843
Effect of Carbon Black on the Development of Oxidation Processes in Raw and Vulcanized Rubbers. A. S. Kuzminskiĭ, L. I. Lyubchanskaya, N. G. Khitrova, and S. I. Bass 858
Influence of Carbon Black on the Oxidation of Natural Rubber. G. J. van Amerongen 862
The Microbiological Deterioration of Rubber Insulation. John T. Blake, Donald W. Kitchin, and Orison S. Pratt 869
Ultrasonic Wave Study of Swollen Buna-N Rubber. A. W. Nolle and J. F. Mifsud 884
Chlorination of Natural Rubber in Solution with Gaseous Chlorine. C. S. Ramakrishnan, D. Raghunath, and J. B. Pande 902
Carbon Black Particle Size. C. H. Leigh-Dugmore 912
Accelerator Compounding. Heat History and Compounding. B. S. Garvey, Jr., D. W. Yochum, and C. A. Morschauser 919
Flex-Cracking and Crack Growth Tests. Some Important Factors. J. M. Buist 935
Rapid Plastometry. J. R. Scott 954
Self-Closing Grips for Rubber. A. J. Stubbs 968
A Study of the Goodrich Flexometer with Synthetic Polymer Compounds. B. G. Labbe 971
Colorimetric Determination of 2-Mercaptobenzothiazole in Compounded Rubber. B. B. Bauminger and F. C. J. Poulton 986

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($4.00 per year) to the Division and thus receive Rubber Chemistry and Technology.

(2) Anyone who is not a member of the American Chemical Society may become an Associate of the Division of Rubber Chemistry upon payment of $6.50 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and libraries may subscribe to Rubber Chemistry and Technology at the subscription price of $7.50 per year.

To these charges of $4.00 and $7.50, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications to become Members or Associates of the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, A. W. Oakleaf, Phillips Chemical Co., 318 Water St., Akron 8, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....J. C. WALTON, Boston Woven Hose & Rubber Co., Cambridge, Mass.
Vice-Chairman.....J. M. BALL, R.F.D. No. 1, Millstone Rd., Wilton, Conn.

Secretary.....A. M. NEAL, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
Treasurer.....A. W. OAKLEAF, Phillips Chemical Co., Akron, Ohio
Editor of *Rubber Chemistry and Technology*....C. C. DAVIS, Boston Woven Hose & Rubber Co., Cambridge, Mass.
Advertising Manager of *Rubber Chemistry and Technology*....E. H. KRISMANN, E. I. du Pont de Nemours & Co., Inc., Akron, Ohio
Directors....S. G. BYAM (Past Chairman), G. R. CUTHBERTSON (Director-at-Large), C. A. RITCHIE (Akron), H. L. HAAS (Boston), C. O. MISERINTINO (Buffalo), A. E. LAURENCE (Chicago), G. R. SPRAGUE (Connecticut), E. J. SIMPSON (Detroit), S. M. YORAN (Fort Wayne), G. W. MILLER (Los Angeles), G. N. VACCA (New York), R. D. FORD (Northern California), T. W. ELKIN (Philadelphia), F. W. BURGER (Rhode Island), J. R. WALL (Southern Ohio), R. E. HARMON (Washington, D. C.).

COUNCILLORS

A. M. NEAL, 1951–4, W. L. SEMON, 1952–5, (Alternates, J. H. FIELDING, 1951–4, H. I. CRAMER, 1952–5).

OFFICERS OF LOCAL GROUPS

AKRON

New officers not reported to RUBBER CHEMISTRY AND TECHNOLOGY.

BOSTON

Chairman....A. W. BRYANT (Binney & Smith Co., Boston). *Vice-Chairman*....W. F. MALCOLM (Titanium Pigment Corp., Boston). *Secretary-Treasurer*....E. D. COVELL (Stedfast Rubber Co., Boston). (Terms expire December 31, 1953.)

BUFFALO

Chairman....RUSS SCHUTZ (U. S. Rubber Reclaiming Co., Buffalo). *Vice-Chairman*....GLENN MEYERS (James Meyers Co., Buffalo). *Secretary-Treasurer*....GENE CIMINELLI (U. S. Rubber Reclaiming Co., Buffalo). (Terms expire December 31, 1953.)

Chicago

New officers not reported to Rubber Chemistry and Technology.

Connecticut

Chairman....Francis J. Rooney (General Electric Co., Bridgeport, Conn.). *Vice-Chairman*....Guy A. Di Norscia (The Sponge Rubber Products Co., Shelton, Conn.). *Secretary*....James R. Boyle (Armstrong Rubber Co., West Haven, Conn.). *Treasurer*....Ward E. Fisher (Armstrong Rubber Co., West Haven, Conn.). (Terms expire December 31, 1953.)

Detroit

Chairman....E. V. Hindle (U. S. Rubber Co., Detroit). *Vice-Chairman*....W. J. Simpson (Chrysler Corp., Detroit). *Secretary*....W. F. Bauer (Brown Rubber Co. Inc., Detroit). *Treasurer*....J. T. O'Reilly (Ford Motor Co., Dearborn). (Terms expire December 31, 1953.)

Fort Wayne

Chairman....D. Reahard, Jr. (General Tire & Rubber Co., Wabash, Indiana). *Vice-Chairman*....C. Coughill, Jr. (Auburn Rubber Co., Auburn, Indiana). *Secretary-Treasurer*....Jack Carlson (Paranite Wire Co., Fort Wayne, Indiana).

Los Angeles

Chairman....D. C. Maddy (Harwick-Standard Chemical Co., Los Angeles 21). *Assoc. Chairman*....L. E. Budnick (Ohio Rubber Co. of Calif., Long Beach). *Vice-Chairman*....F. C. Johnston (Caram Mfg. Co., Monrovia). *Secretary*....Carl Hoglund (R. D. Abbott Co., Los Angeles 22). *Treasurer*....Roy N. Phelan (Atlas Sponge Rubber Co., Los Angeles). (Terms expire January 1, 1954.)

New York

Chairman....G. N. Vacca (Bell Telephone Laboratories, Murray Hill, N. J.). *Vice-Chairman*....Joseph Breckley (Titanium Pigment Corp., New York). *Secretary-Treasurer*....B. B. Wilson (*India Rubber World*, New York). (Terms expire December 31, 1953.)

Northern California

Chairman....J. N. Hollister (Mare Island Naval Shipyard, Vallejo). *Vice-Chairman*....William Moser (Facific Tire and Rubber Co., Oakland). *Secretary*....Halsey C. Burke (Burke Rubber Co., San Jose). *Treasurer*....Eugene Gador (Oliver Tire and Rubber Co., Oakland). (Terms expire December 31, 1953.)

Philadelphia

Chairman....G. J. Wyrough (Wyrough & Loser, Trenton, N. J.). *Vice-Chairman*....A. J. Dimaggio (Firestone Tire and Rubber Co., Pottstown, Pa.). *Secretary-Treasurer*....M. A. Youker (E. I. du Pont de Nemours & Co., Wilmington, Del.). (Terms expire January 1954.)

RHODE ISLAND

New officers not reported to RUBBER CHEMSITRY AND TECHNOLOGY.

SOUTHERN OHIO

Chairman....GEORGE E. LANG (Johnson Rubber Co., Middlefield). *Vice-Chairman*....STEWART L. BRAMS (Dayton Chemical Products Laboratories, Inc.). *Secretary*....RUSSELL J. HOSKIN (Inland Mfg. Div., G. M. Corp., Dayton). *Treasurer*....WM. L. NOLAN (Inland Mfg. Div., G. M. Corp., Dayton). (Terms expire December 31, 1953.)

WASHINGTON, D. C.

Chairman....GEORGE M. RIVEIRE (Goodyear Tire & Rubber Co.). *Vice-Chairman*....PAUL GEER (Office of Synthetic Rubber, RFC). *Secretary*....ALFRED M. ANISMAN (Office of Synthetic Rubber, RFC). *Treasurer*.... ETHEL LEVINE (Bureau of Ships, Navy Department). (Terms expire October 1954).

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY, LOS ANGELES, CALIF., MARCH 18 AND 19, 1953

The 62nd Meeting of the Division of Rubber Chemistry was held in Los Angeles, March 18 and 19, in conjunction with the 123rd national meeting of the American Chemical Society. Headquarters were at the Hotel Statler, and the attendance was 208.

The following papers were presented:

Aging Characteristics of Crude Guayule Rubber. W. J. GOWANS AND F. E. CLARK (Natural Rubber Research Station, United States Department of Agriculture, Salinas, Calif.).

An Improved Method of Determining Rubber Hydrocarbon in Rubber-Bearing Plants. J. W. MEEKS, R. V. CROOK, C. E. PARDO, JR., AND F. E. CLARK (Natural Rubber Research Station, United States Department of Agriculture, Salinas, Calif.).

Some Recent Developments in Polymerization of GR–S at Low Temperatures. L. H. HOWLAND, V. C. NEKLUTIN, R. L. PROVOST, AND F. A. MAUGER (Naugatuck Chemical Division, U. S. Rubber Co., Naugatuck, Conn.).

Chemical Nature of Extenders and Their Standardization for Use In Oil-Extended Rubbers. FRITZ S. ROSTLER AND R. M. WHITE (Golden Bear Oil Co., Oildale, Calif.).

High-Styrene Resin Reinforcement of Hard-Rubber Stocks. H. S. SELL AND R. J. MCCUTCHEON (Goodyear Tire & Rubber Co., Akron, O.).

Modern Vulcanization Processes. H. A. FREEMAN (Goodyear Tire & Rubber Co., Akron, O.).

Variables in the Compounding of Resin Acid-Rubber Masterbatches. J. F. SVETLIK AND R. S. HANMER (Phillips Petroleum Co., Bartlesville, Okla.).

Derivatives of Chlorosulfonated Polyethylene and Their Infrared Spectra. M. A. SMOOK, E. T. PIESKI AND C. F. HAMMER, (E. I. du Pont de Nemours & Co., Wilmington, Del.).

Chemical Resistance of Chlorosulfonated Polyethylene. R. T. CURRIN (E. I. du Pont de Nemours & Co., Wilmington, Del.).

Statistical Methods in Compounding Chlorosulfonated Polyethylene. W. L. Gore (E. I. du Pont de Nemours & Co., Wilmington, Del.).

Influence of Various Weathering Factors on Ozone Cracking of Natural and Synthetic Rubbers. W. G. Mayes (Firestone Tire & Rubber Co., Akron, O.).

Ozone Formation in the Photochemical Oxidation of Organic Substances. A. J. Haagen-Smit and C. E. Bradley (California Institute of Technology, Pasadena, Calif.) and M. M. Fox (Los Angeles County Air Pollution Control District, Los Angeles, Calif.).

The Structure of Neoprene. VI. Crystallization. J. T. Maynard and W. E. Mochel (E. I. du Pont de Nemours & Co., Wilmington, Del.).

Program in Rubber Technology at the University of Southern California. R. E. Vivian and J. S. Smatko (University of Southern California, Los Angeles).

Powdered Reclaim. D. S. le Beau (Midwest Rubber Reclaiming Co., East St. Louis, Ill.).

A Simple Flexibility Test. D. G. Stechert (Gates Rubber Co., Denver, Colo.).

Chemistry in Carbon Black Dispersion. B. C. Barton and G. H. Ganzhorn (U. S. Rubber Co., Passaic, N. J.).

The Ultimate Analyses of Carbon Blacks. I. Merton Studebaker (Phillips Chemical Co., Akron, O.).

The Ultimate Analyses of Carbon Blacks. II. Merton Studebaker (Phillips Chemical Co., Akron, O.).

The Effect of Temperature on Thermal Conductivity Coefficient of Silicone Rubber Compounds. M. G. Etzwiler, R. M. Combs, and T. J. Sobol (Connecticut Hard Rubber Co., New Haven, Conn.).

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY, BOSTON, MASS., MAY 27 TO 29, 1953

The 63rd Meeting of the Division of Rubber Chemistry was held in Boston, May 27–29, 1953, with headquarters at the Hotel Statler. The meeting was attended by 1014 members and guests.

The 25-Year Club met under the Chairmanship of William B. Kavenagh, with 196 present. H. P. Fuller of the Boston Group and C. R. Haynes, Secretary of the Division, were tied in the contest for the longest service in the rubber industry.

The Pops Concert at Symphony Hall was taken over by the Division, A. W. Bryant in charge, and the program was enthusiastically received by all present.

At the Banquet there were approximately 1000 guests, and in a short ceremony recognizing the achievements of C. C. Davis as editor for twenty-five years of Rubber Chemistry and Technology he was presented with a silver bowl. Announcement was made of John T. Blake as Goodyear Medalist for 1953. Harry A. Winnie, a Vice-President of the General Electric Company, spoke on "Energy from the Atom." Wally Cox, known as "Mr. Peepers" on television, also spoke.

At the Business Meeting, recognition was made of the deaths since the last meeting of E. G. Cashman, E. G. Croakman, E. C. Dill, G. L. Hammond, D. A. Shirk, and H. M. Smallwood.

The following papers were presented:

Effect of Variations of Oil Composition on Physical Properties of Cured Effect Masterbatched Polymer Compounds. W. K. Taft, R. W. Laundrie, J. Duke, and A. D. Snyder (Government Laboratories, University of Akron, Akron, O.).

Effect of Type of Oil Used in Masterbatching on Molecular Structure of Polymer. W. K. Taft, J. Duke, R. W. Laundrie, A. D. Synder, and D. C. Prem (Government Laboratories, University of Akron, Akron, O.).

Factors Influencing Polymer Breakdown. W. K. Taft, J. Duke, A. D. Snyder, D. C. Prem, and H. Mooney (Government Laboratories, University of Akron, Akron, O.).

Chromatographic Separation of Rubber-Processing Oils from Petroleum Sources. T. F. Mika, F. M. McMillan, and S. H. Page (Shell Development Co., Emeryville, Calif.).

Petroleum Oil Extenders—Correlation of Properties in GR–S with Chromatographic Analysis. W. L. Dunkel, F. P. Ford, and J. H. McAteer (Chemical Division, Esso Laboratories, Standard Oil Development Co., Elizabeth, N. J.).

Superfast 41°F GR–S Polymerization Recipes. J. R. Miller (B. F. Goodrich Chemical Co., Cleveland, O.).

Gelation of 41°F GR–S and Nitrazole-CF Initiated (122°F) Polymer as a Result of High-Temperature Mastication. Glen Alliger, W. S. Cook, and R. D. Wolfangel Firestone Tire & Rubber Co., Akron, O.).

Physico-Chemical and Rubber Reinforcing Properties of Super-Abrasion Furnace Black. J. F. Svetlik, H. E. Railsback, and C. C. Biard (Phillips Petroleum Co., Bartlesville, Okla.).

The Effect of Carbon Black on the Oxidation of Unvulcanized Cold Rubber. F. Lyon, K. A. Burgess, and C. W. Sweitzer (Columbian Carbon Co., New York, N. Y.).

Oxidation and Antioxidant Action in Rubber Vulcanizates. J. Reid Shelton and W. L. Cox (Case Institute of Technology, Cleveland, O.).

Migration of Materials Between Samples in Accelerated Aging Ovens. R. N. Thomson and N. S. Grace (Dunlop Tire & Rubber Goods Co., Ltd., Toronto, Canada).

Heat-Aging Characteristics of Chlorosulfonated Polyethylene. W. J. Remington (Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

The Structure of Neoprene. VII. Infrared Analysis of Configuration. J. T. Maynard and W. E. Mochel (Chemical Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

Chemigum-SL—An Elastomeric Polyester-Urethane. N. V. Seeger, T. G. Mastin, E. E. Fauser, F. S. Farson, and E. A. Sinclair (Goodyear Tire & Rubber Co., Akron, O.).

Compounding Neoprene for Increased Resistance to Water. C. E. McCormack, R. H. Baker, and R. S. Graff (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

Fundamental Low-Temperature Retraction Studies of Natural and Synthetic Elastomers. L. J. Radi and N. G. Britt (Interchemical Corp., New York, N. Y.).

Determination of Particle-Size Distribution in GR–S Latexes. A. Nisonoff, W. E. Messer, and L. H. Howland (Naugatuck Chemical Division, U. S. Rubber Co., Naugatuck, Conn.).

Rheology of Latex and Latex Compounds. LOUIS LEAMAN (Magic Chemical Co., Brockton, Mass.).

A Paper Dip Method for Measuring Wet Gel-Strength of Coagulant Dipped Films. A. I. MEDALIA AND H. B. TOWNSEND (Boston University, Boston, Mass.).

Aging Stability of Neoprene Latex. D. E. ANDERSEN AND R. G. ARNOLD (E. I. du Pont de Nemours & Co., Wilmington, Del.).

Titer Compounding of Neoprene Latex. G. S. COOK AND J. C. FITCH (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

The Relation Between Soluble Polymer in Chloroprene Monomer and the Mechanical Stability of Neoprene Latex. N. G. O'BRIEN, J. R. GOERTZ, AND R. A. HAMMOND (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY CHICAGO, ILLINOIS, SEPTEMBER 9 TO 11, 1953

The 64th Meeting of the Division of Rubber Chemistry was held in Chicago, September 9 to 11, 1953, with headquarters at the Hotel Sherman. There was a registration of 800 members and guests.

The 25-Year Club met at luncheon, with H. A. Winkelmann as chairman. Frank Malm, with the longest service in the industry, 46 years, was honored. The Banquet was held on Thursday evening, September 10, at which time the Goodyear Medal was presented to John T. Blake. Special tribute was paid to C. R. Haynes, who retired as secretary of the Division.

Future meetings will be in Louisville, Ky., April 14–16, 1954, in New York City, September 15–17, 1954, in Detroit, May 4–6, 1955, and in Philadelphia, November 2–4, 1955.

At the Business Meeting, M. E. Lerner, Chairman of the Ballot Committee, announced the result of the election of officers and directors: Chairman, J. C. Walton; Vice-Chairman, J. M. Ball; Secretary, A. M. Neal; Treasurer, A. W. Oakleaf. Directors: Director-at-Large: G. R. Cuthbertson; G. R. Sprague, *Connecticut;* E. J. Simpson, *Detroit;* R. D. Ford, *Northern California;* T. W. Elkin, *Philadelphia;* F. W. Burger, *Rhode Island;* J. R. Wall, *Southern Ohio:* R. E. Harmon, *Washington, D. C.*

The following papers were presented:

Flame Photometric Determination of Rubber Solids Deposited on Cords and Fabrics. H. E. TODD AND H. M. TRAMUTT (Gates Rubber Co., Denver, Colo.).

A Tracer Method for Sulfur Solubility in Rubber. I. AUERBACH AND S. D. GEHMAN (Goodyear Tire & Rubber Co., Akron, O.).

The Effect of Heat Treatment on the Reinforcing Properties of Carbon Black. W. D. SCHAEFFER AND W. R. SMITH (Research and Development Laboratories, Godfrey L. Cabot, Inc., Boston, Mass.).

The Adsorption of Iodine and Bromine by Carbon Black. J. W. WATSON AND D. PARKINSON (Research Center, Dunlop Rubber Co., Ltd., Birmingham, England).

Extrusion Factors of Black Rubber Compounds. ISAAC DROGIN, H. R. BISHOP, AND PAUL WISEMAN (United Carbon Co., Charleston, West Va.).

Experimental Blacks for Rubber Compounds. A. G. COBBE, M. POLLEY, AND J. S. BOYD (Cabot Carbon Co., Pampa, Texas).

The Effect of Various Surface Treatments on the Reinforcement and Rate of Cure of Silica-Loaded Stocks. W. R. Hausch (Firestone Tire & Rubber Co., Akron, O.).

Vulcanization Characteristics of a Series of 4-Methyl-5-Substituted 2-Thiazolethiols and Their Derivatives. J. J. D'Amico, K. E. Creed, Jr., M. W. Harman, and R. O. Zerbe (Monsanto Chemical Co., Nitro, West Va.).

Compounding with Lignin and Humic Acid. F. J. Tibenham (Dunlop Rubber Co., Ltd., Birmingham, England) and N. S. Grace (Dunlop Tire & Rubber Goods Co., Ltd., Toronto, Canada).

Mechanism of Vulcanization of Polysulfide Rubber. E. M. Fetters, J. R. Panek, and J. S. Jorczak (Thiokol Chemical Corp., Trenton, N. J.).

A New Unvulcanized Composition of Resin and Rubber Having Unusual Toughness. H. S. Sell and R. J. McCutcheon (Goodyear Tire & Rubber Co., Akron, O.).

Comparison of Methods of Accelerated Aging of Latex Foam Rubber. T. H. Rogers and H. H. Heineman (Goodyear Tire & Rubber Co., Akron, O.).

Load-Carrying Capacity of Latex Foam Rubber. J. A. Talalay (Sponge Rubber Products Co., Shelton, Conn.).

Charles Goodyear Lecture: The Future of Rubber. J. T. Blake (Simplex Wire & Cable Co., Cambridge, Mass.).

High-Polymer Training and Research at the University of Michigan. L. M. Hobbs (University of Michigan, Ann Arbor, Mich.).

Mercaptans (Thiols) in Polymerizations: A Review with Recent Developments. A. H. Krause (Kentucky Synthetic Rubber Corp., Louisville, Ky.).

Molecular Weights of Emulsion Polydienes. Maurice Morton (Government Laboratories, University of Akron, Akron, O.).

Sodium Formaldehyde Sulfoxylate as Reducing Agent in Low-Temperature GR–S Polymerization. R. W. Brown, C. V. Bawn, E. B. Hansen, and L. H. Howland (Naugatuck Chemical Division, U. S. Rubber Co., Naugatuck, Conn.).

Non-Discoloring Stabilizers for GR–S. B. A. Hunter, R. R. Barnhart, and R. L. Provost (Naugatuck Chemical Division, U. S. Rubber Co., Naugatuck, Conn.).

Solution Coatings of Chlorosulfonated Polyethylene. R. D. Sudekum (Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

Blends of Chlorosulfonated Polyethylene with Butadiene-Acrylonitrile Copolymers. F. F. Holub, R. A. Hutchinson, and W. J. Remington (Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

Adhesives for Chlorosulfonated Polyethylene. G. H. Bowers, I. D. Roche, and R. C. Baker (Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.).

NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1952. Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W. 1, England, 7 × 9¼ in. 166 pp. £1 1s 0d (approximately $3.00).—The latest edition of this valuable annual report covers developments in all branches of the rubber field which occurred within the calendar year of 1952. As usual, the reports were prepared by outstanding authorities and experts, with special reports devoted to statistics, cultivation, physics and chemistry, testing equipment, compounding ingredients, latex, synthetic rubber, cellular rubber, hard rubber, machinery and appliances, various types of rubber products, etc. The current edition is marked by the restoration of a report on "Works Processes and Materials" by H. W. Badger and the initiation of a report on "Roads" by L. Mullins and A. R. Smee. Although the latter report is only two and a half pages in length, it indicates the importance of the growing use of rubber in roads. As usual, author and subject indexes are included, credit for which is due to Dr. Drakeley. [From *The Rubber Age* of New York.]

SYMPOSIUM ON RECENT DEVELOPMENTS IN THE EVALUATION OF NATURAL RUBBER. (Technical Publication No. 136.) Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 120 pp. $2.25.—Eight papers devoted to recent developments in the evaluation of natural rubber were presented in a special symposium sponsored by ASTM Committee D-11 on Rubber and Rubberlike Materials at the 1952 Annual Meeting of the Society held in New York City. The program was developed by Subcommittee XII on Crude Natural Rubber, of which Norman Bekkedahl, of the National Bureau of Standards, is chairman. Titles and authors of the papers, all of which are reproduced in this booklet together with the subsequent discussion, follow:

(1) Technical Classification of Crude Natural Rubber, by R. G. Newton; (2) Quantitative Procedures for the Determination of Dirt in Crude Natural Rubber, by R. P. Stock, C. O. Miserentino, C. B. McKeown, J. J. Hoesly, R. T. LaPorte, and G. H. Wallace; (3) Mooney Viscosity Measurements in Determining Processibility of Technically Classified Rubbers, by Rolla H. Taylor and Alan G. Veith; (4) Technically Classified Rubber—The Nonrubber Content and the Measurement of Cure Rate, by A. G. Veith; (5) Vulcanization Characteristics of Natural Rubber, by Robert D. Stiehler and Frank L. Roth; (6) Preparation of a Standard Natural Rubber, by E. M. McColm; (7) Some aspects of the Testing of Crude Rubber and Crude Rubber Compounds, by L. V. Cooper and T. M. Kersker; (8) Rubber Evaluations with the Instron Testing Machine, by S. D. Gehman and R. P. Clifford. An introduction to the symposium by Mr. Bekkedahl is also included in the booklet. [From *The Rubber Age* of New York.]

THE NEOPRENES. Principles of Compounding and Processing. Neil L. Catton. E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. Cloth, 6 by 9 inches, 260 pages. Illustrations, appendixes, subject index.—As the author explains in his foreword, much investigative work, done in the two decades since Neoprene became commercially available, has appeared in scien-

tific and trade publications and in du Pont technical literature. "The Neoprenes" has been compiled to assemble the results in one volume as a reference book for the technologist and a textbook for young men in the rubber industry. The book concerns itself with the fundamental principles of compounding and processing all types of dry Neoprene, and is amply documented and illustrated. The appendixes contain useful information applicable to all types of elastomers.

The book is in five parts, the first four of which concern types of Neoprene, general-purpose Neoprenes, special-purpose Neoprenes, and vulcanizate properties.

The author has followed a fairly regular and convenient procedure with most of the Neoprenes by first listing the physical and chemical properties, followed by basic compounding formulations, vulcanization procedures, and then covering the effects of filler loading, plasticizer addition, etc. Compounding for special properties is then detailed, and processing procedures are outlined.

Vulcanizate properties is reported mostly by graphs and should be of particular value for easy ready reference. Appendixes, include additional details on storage stability of Neoprene, Banbury mixing, calendering set-ups, blends of Neoprene with other elastomers, etc. [From the *India Rubber World.*]

GOMMA ELASTICA: CHIMICA E TECNOLOGIA. 6. Piantanida. Casa Editrice Dottore Carlo Cya, Florence, Italy. 1952. 381 pages.—This general treatise, written by specialists, attempts to fill a gap in the Italian literature. It comprises the following subjects: history; processing; compounding ingredients; mechanical properties; machinery; organization of a factory; industrial techniques; pneumatic tires and air bags; belting; sport goods; cables and conductors; laboratory tests and research methods; synthetic rubber; ebonite; industrial statistics. There is no bibliography. (From *Revue Générale du Caoutchouc.*]

HANDBOOK OF MATERIAL TRADE NAMES. 1953 Edition. O. T. Zimmerman and Irvin Lavine. Published by Industrial Research Service, Masonic Bldg., Dover, N. H. Cloth, 7¼ by 10¼ inches, 810 pages. Price: $20 domestic; $22.50 foreign. Rather than a new edition of the original 1946 handbook, this volume is a completely new book, since it has been entirely rewritten, greatly expanded, and improved by the addition of new features. The title is misleading, since the book covers material trade names, registered and unregistered trade marks, common names, and generic terms, each identified by a distinguishing symbol. The text is divided into three sections. The first is an alphabetical listing of more than 15,000 materials; each entry gives the properties, important uses, and manufacturer of the product. The second section is a cross-indexed classification of the materials according to their compositions and uses. The concluding section offers the names and the addresses of the more than 1,500 firms mentioned in the book, together with a list of each company's products. [From the *India Rubber World.*]

HANDBOOK OF CHEMISTRY AND PHYSICS. Thirty-fourth Edition. Charles D. Hodgman, Editor-in-Chief. Chemical Rubber Publishing Co., 2310 Superior Ave. N.E., Cleveland, O. Cloth, 4½ by 7¼ inches, 2,970 pages. Price, $8.50.—This new edition of the Handbook retains the format and general appearance of the preceding issues and divides the contents into five sections: mathematical tables; properties and physical constants; general chemical

tables; physics data; and quantities and units. In addition to numerous changes throughout the data, two major revisions involving the addition of 274 pages have been made by resetting the tables on physical constants of inorganic compounds, and physical constants, of industrial organic compounds. The table on physical properties of natural and synthetic rubber stocks has been completely revised and brought up to date, and considerable data have been added to the table of constants of oils, fats, and waxes. [From the *India Rubber World.*]

CROSS-LINKING IN NATURAL-RUBBER VULCANIZATES *

H. E. Adams and B. L. Johnson

Chemical and Physical Research Laboratories, the Firestone Tire and Rubber Co., Akron, Ohio

Recently, a method for measuring the average number of cross-links per chain of vulcanized polymer has been developed[1]. It is possible to calculate the degree of cross-linking of the vulcanizate from its amount of swelling in a solvent such as benzene. This method was used by Flory[2] to study the effect of primary molecular weight on the cross-linking of Butyl vulcanizates. An evaluation of the general validity of the method was ascertained by using quantitative cross-linking agents (diazodicarboxylates) to prepare vulcanizates of natural rubber and GR-S[3]. Bardwell and Winkler[4] have also used this technique to study the relationship between the degree of cross-linking and the force of retraction at 300 per cent elongation of GR-S latex vulcanized with potassium persulfate.

The formation of cross-linking during the vulcanization by sulfur of several polymers has also been investigated. Gee[5] has compared the formation of cross-linking in natural rubber vulcanizates with the amount of combined sulfur. Carbon-to-carbon cross-links were believed to be formed in a nonsulfur tetramethylthiuram disulfide (TMTD) cure. A similar study of Butyl rubber vulcanizates, cured with sulfur-TMTD, indicates that disulfide cross-links are formed[6]. Scott and Magat[7] have estimated that eight sulfur atoms are associated with each cross-link in Russian SK (sodium polybutadiene)[8]. This investigation was undertaken to extend Gee's study[5] on the correlation of the cross-linking of natural-rubber vulcanizates with the amount of combined sulfur.

It is possible to calculate the degree of cross-linking from the amount of equilibrium swelling according to the theory of Flory and Rehner[9]. However, to do this, the value of μ, the interaction constant between the rubber and the swelling medium, must be accurately known. Equation 1 relates the molecular weight between cross-links, M_c, with the volume fraction[9] of rubber in the swollen vulcanizate, v_r:

$$\nu = \frac{1}{M_c} = \frac{v_r + \mu v_r^2 + 2.303 \log (1 - v_r)}{\rho_r V_0 (v_r^{\frac{1}{3}} - v_r/2)} \tag{1}$$

The network-statistical theory of rubber elasticity[10] leads to the following expression for the force of retraction, f, in stretched rubber as a function of temperature, elongation, and network structure:

$$f = \frac{\rho_r A_0 RT}{M_c} \left(\alpha - \frac{1}{\alpha^2} \right) \tag{2}$$

where α is the length of the stretched rubber relative to its unstretched length. This expression has been found to be only approximately correct. Recently,

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 7, pages 1539–1546, July 1953. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at a meeting in Buffalo, N. Y., October 29–31, 1952.

Gee[11] has studied the tensile properties of rubbers in the swollen state, and has found that the above expression is more nearly valid if the rubber is in the swollen state. Equation 2 then has to be modified to the following form:

$$f = \frac{\rho_r A_0 RT}{M_c} \beta \left(\alpha - \frac{1}{\alpha^2} \right) \tag{3}$$

where α is now the ratio of the stretched swollen length to the unstretched swollen length. This, then, provides a method for calculating M_c from the slope of the line obtained by plotting f/A_0 against $(\alpha - 1/\alpha^2)$.

MEASUREMENT OF CROSS-LINKING

Tension method.—In order to study the elastic properties of rubbers in the partially swollen state, an apparatus similar to the one used by Gee[11] was constructed. It is shown schematically in Figure 1. It was constructed so that the extension at various loads could be measured.

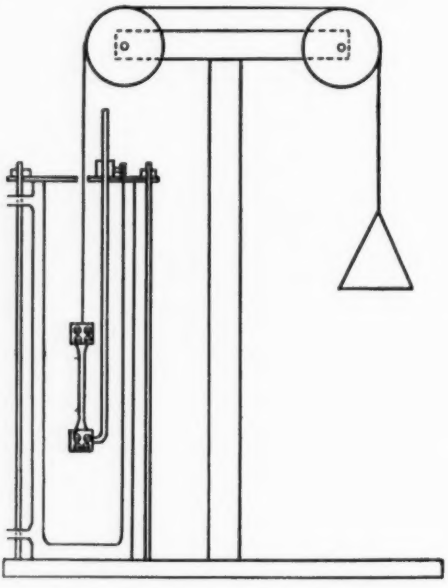


FIG. 1.—Apparatus for tension measurements.

The test-specimen is mounted in two clamps, one of which is attached to a long fixed rod, the other fastened directly to a steel tape that passes over two pulleys. These two low-friction pulleys are mounted on a rigid beam. The test-specimen held by the clamps is placed in a double-walled glass container. The rod fastened to the lower clamp runs through a block on the metal lid of the container. By means of a setscrew, this rod may be adjusted to any height, thus fixing the extension of the rubber tensile strip. Water from a constant temperature bath is circulated through the outer jacket in order to maintain the test-specimen at a definite temperature. Inert liquids or liquids capable of

swelling the rubber can be put in the inside container surrounding the test strip. The amount of extension was measured by means of a cathetometer.

The following experimental procedure was used to determine the elastic properties of the partially swollen natural rubber stock:

Tensile strips were cut from the cured slabs, and two small pieces of piano wire were inserted into the neck of the strip to serve as bench-marks. The distance between these two wires, measured by means of a cathetometer, served as the initial length. The strips were swollen in benzene containing a small amount of phenyl-β-naphthylamine for a period of 2½ hours. These swollen samples were then placed in water saturated with benzene for at least 3 days, so that the sample would equilibrate and the degree of swelling become uniform throughout the strip. At the end of this time, the samples were placed in the clamps of the apparatus.

All the manipulations were carried out beneath the surface of water in order to minimize the loss of imbibed benzene, due to evaporation. During the actual measurement, the sample is immersed in water saturated with benzene, the temperature maintained at 25° C. After allowing sufficient time for the sample to come to constant temperature, the distance between the two wires is again measured. This determines the amount of swelling that has occurred. The sample is then extended by means of weights to approximately 100 per cent, the maximum amount of extension that can be tolerated for any length of time without breaking the sample. This extension was maintained for ½ hour before a reading of the extension was taken. Then the extension was reduced in a series of steps by removing the proper weight. Before taking a reading, 5 minutes were allowed to elapse. Finally, the distance between the two wires was redetermined with zero load. This distance never deviated from the original length by more than 2 per cent, which indicates that negligible creep took place. A much longer, time-consuming routine was employed on one of the samples and the results were compared with those obtained by the usual method. Within experimental error, identical results were obtained.

The average number of cross-linked units was calculated by means of the following equation:

$$\nu = \chi \times 10^{-4}/2324 \tag{4}$$

where χ is defined by the following expression:

$$\chi = \frac{f}{A_0} \frac{1}{\beta \left(\alpha - \frac{1}{\alpha^2} \right)} \tag{5}$$

Thus, the general reliability of Equation 3 can be tested. If the equation fits the data, χ should be a constant, regardless of the value of the elongation, α.

Three stocks of natural rubber compounded in the ACS gum formula were cured at 280°, 300°, and 320° F for various periods of time. Stress-strain data were obtained for these three stocks in the partially swollen state. In addition, stress-strain data for the dry stock cured at 280° F were obtained. Figure 2 contains these results plotted in the form of χ versus 100 $(\alpha - 1)$. These curves are to be compared with the straight lines obtained in Figure 3 for the stress-strain data of the same stock in the partially swollen state. This comparison illustrates, very nicely, the improvement obtained in the fit of the theoretical equation to data of the partially swollen vulcanizate. Secondary valence forces are apparently inoperative in the swollen stock and the retractive force is dependent only on the primary bonds of the network structure.

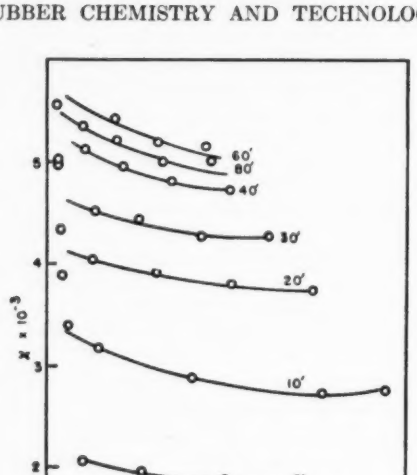


FIG. 2.—Variation of χ with extension for unswollen natural rubber vulcanizates.

Composition, parts per 100 parts rubber

Sulfur	3.5
MBT	0.5
Stearic acid	0.5
Zinc oxide	6.0

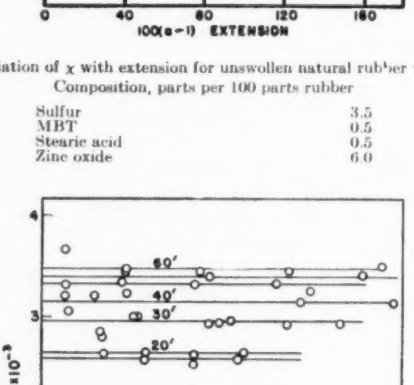


FIG. 3.—Variation of χ with extension for partially swollen natural rubber vulcanizates.

Composition, parts per 100 parts rubber

Sulfur	3.5
MBT	0.5
Stearic acid	0.5
Zinc oxide	6.0

Equilibrium swelling method.—The other method for determination of the amount of cross-linking is that of equilibrium swelling. The experimental technique is very simple.

Small squares, 0.5 × 0.5 inch, were cut from the cured slabs (0.075 inch thick) and weighed in duplicate. These squares were then swollen in benzene, which contained a small amount of phenyl-β-naphthylamine, for a period of 48 hours. This time period had been determined to be sufficient for equilibrium swelling to occur. Slight additional swelling occurred after this period because of oxidation of the vulcanizate by the air. This has been designated as the increment swelling by Scott[12]. The correction for this increment swelling over a period of 48 hours is negligible and was not applied. The swollen samples were removed from the benzene and weighed in stoppered weighing bottles after the excess benzene had been removed by blotting the wet samples with filter paper. The imbibed benzene was removed by evaporation in an oven at 70° C overnight. The dried samples were then weighed to determine the amount of each sample which had dissolved in the benzene. The amount of swelling, Q, was calculated by means of the following expression:

$$Q = \frac{\rho_r}{\rho_s}\left[\frac{\gamma - 1 + s}{F - s}\right] \tag{6}$$

Here, Q is defined as the number of milliliters of solvent imbibed by 1 cc. of rubber. A slight inaccuracy is inherent in the results because of the unknown composition of the dissolved fraction. Equation 6 assumes that the dissolved fraction is 100 per cent rubber. The volume fraction of rubber, v_r, is related to the swelling according to the following equation:

$$v_r = 1/1 + Q \tag{7}$$

Since there is some question of the validity of the general application of these methods for the determination of cross-linking in sulfur-cured vulcanizates, the following procedure, which affords a partial check on the validity of the method, was followed. Values of the molecular weight between cross-links were calculated from the tension measurements and substituted in Equation 1, along with values of v_r for the same vulcanizate determined from the amount of equilibrium swelling. A value of μ for each vulcanizate was calculated for a total of 50 natural rubber stocks. This includes stocks which contained a variation in sulfur content of 0 to 25 per cent and stocks with various amounts of accelerators, such as TMTD and mercaptobenzothiazole (MBT). The average value of μ in the case of natural rubber is 0.437 ± 0.010. This agrees very well with the results of Huggins[13], where μ = 0.43 to 0.44, but is in poor agreement with Gee's value[5] of μ = 0.396. By using a single reasonable value for the constant, μ, good agreement in the cross-linking is obtained by the two independent measurements, which tends to establish the general validity of the methods.

Of course it must be remembered that the quantity measured is the effective number of cross-linked units, ν, which is related to the actual cross-linking, n_0, and primary molecular weight, M_n, as follows:

$$\nu = \frac{1}{M_c} = 2n_0 - \frac{2}{M_n} \tag{8}$$

In the case of natural rubber, it was assumed that M_n is sufficiently high so that the free end fraction is negligible and can be neglected. Then:

$$n_0 = \nu/2 \tag{9}$$

SULFUR DETERMINATION

Combined Sulfur.—The method used for the determination of the combined sulfur is essentially that of Kelly[14]. The sample is successively extracted with acetone, alcoholic potassium hydroxide, alcohol, and hydrochloric acid-ether to remove noncombined sulfur. The sulfur content (wet oxidation method) of the extracted sample is then taken as the amount of combined sulfur.

Sulfide Sulfur.—The proportion of sulfide sulfur in the vulcanizates was determined by a method based on that of Stevens[15], with several modifications. The all-glass apparatus, shown in Figure 4, was used for this determination.

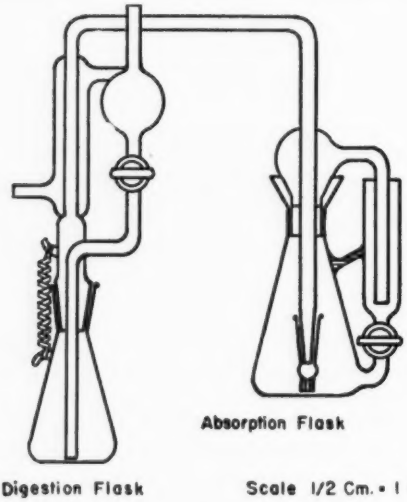


FIG. 4.—Apparatus for determination of mineral sulfide content.

The sample, along with 25 cc. of freshly distilled ether, was placed in the digestion flask. The presence of peroxides in the ether was shown to give low and erratic values of the amount of mineral sulfide present in the vulcanizate. The apparatus was then assembled and mounted so that the reaction flask was immersed in a constant temperature water bath maintained at 37° C. Absorbing solution (5.0 grams of cadmium chloride, 25 grams of sodium acetate, and 25 cc. of concentrated acetic acid per liter of solution)[16] was placed in the main section and side arm of the absorption flask. After the sample had become swollen with ether (1 hour), 25 cc. of concentrated hydrochloric acid was added to the digestion flask, and nitrogen was bubbled fairly rapidly through the reaction mixture for a period of 1 hour. At the end of this time, the nitrogen was shut off and the absorption flask, along with the removable tip of the delivery tube, was detached from the apparatus and tightly stoppered.

The amount of hydrogen sulfide liberated from the sample by the hydrochloric acid-ether digestion was absorbed as cadmium sulfide in the absorbing solution. The amount of cadmium sulfide formed was determined[17] by iodine oxidation of the sulfide. Thirty ml. of concentrated hydrochloric acid and 10 cc. of 10 per cent potassium iodide solution were added to the cadmium sulfide precipitate. Immediately, the solution was titrated to a slight excess with 0.025 *N* potassium iodate solution. The excess iodate was titrated with 0.015 *N* sodium thiosulfate solution. By adjustment of the size of the sample of vulcanizate, the amount of hydrogen sulfide liberated in the titration was always less than 0.25 milliequivalents. This eliminated the loss of hydrogen sulfide during the titration.

CURING COMPONENTS AND CROSS-LINKING

This paper is limited to the study of natural-rubber vulcanizates. Furthermore, the study, with two exceptions, involves MBT-accelerated sulfur cures. Vulcanizates containing variable amounts of the three necessary curing components, *viz.*, sulfur, accelerator, and soluble zinc, were prepared by the usual

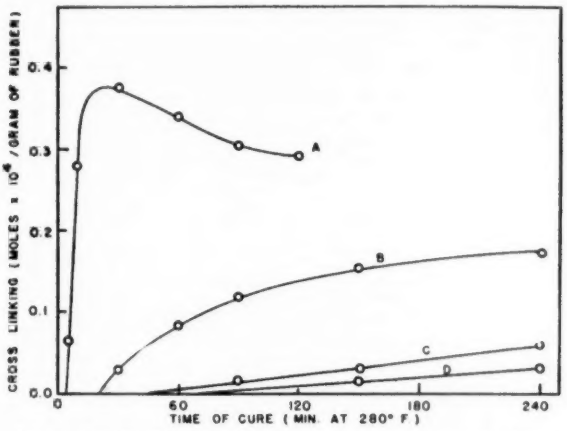


FIG. 5.—Specific effect of individual curing ingredients on cross-linking.

	Composition, parts per 100 parts rubber		
	Sulfur	MBT	Zinc stearate
A	2	1	6
B	2	1	
C	2		
D	2		6

laboratory techniques. Soluble zinc was added to the vulcanizate by two methods. In one case, zinc oxide and stearic acid were added together; in the other method an organic salt of zinc was added. Usually zinc stearate was used, but zinc propionate, zinc lactate, zinc oxalate, and zinc benzoate also were tried. The solubility of zinc lactate and zinc oxalate in rubber was so small that insufficient zinc was introduced to secure a satisfactory cure. The specific composition of the individual vulcanizates will be indicated on the appropriate graphs.

Figure 5 illustrates the specific effects of the individual curing ingredients on the rate of formation of cross-links at 280° F. All the vulcanizates contained 2

parts of sulfur per 100 parts rubber. Although the rate of formation of cross-links in the vulcanizate which contained sulfur alone is very slow, the addition of zinc stearate reduced this rate still further. Since an appreciable amount of zinc sulfide was formed in the zinc-containing vulcanizate, it is possible that hydrogen sulfide[18] may play an important part in the cross-linking reaction of straight sulfur cures. The absorption of hydrogen sulfide by the zinc would

TABLE I

INDIVIDUAL CURING INGREDIENTS

Compn., parts per 100 parts rubber			Moles of Cross-linked units $\times 10^4$/g. rubber	Atoms of combined sulfur $\times 10^4$/g. rubber
Sulfur	Zinc stearate	MBT		
2	0	0	0.132	2.04
2	6	0	0.062	1.42
2	0	1	0.350	5.74
2	6	1	0.679	5.04

interfere with its addition to the unsaturation of the rubber molecule and thus retard the formation of cross-links.

The inclusion of MBT, in addition to sulfur, somewhat increases the rate of formation of cross-links. However, this increase in cross-linking is about equal to that obtained in a straight sulfur cure at the same amount of combined sulfur. The most spectacular change is obtained by using the combination of sulfur, MBT, and zinc stearate. The increase of the rate of cross-linking is also ac-

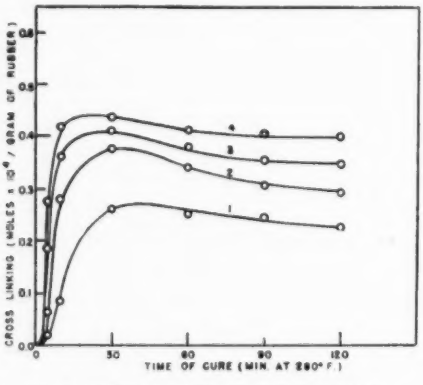


FIG. 6.—Effect of sulfur content on cross-linking.

Composition, parts per 100 parts rubber	
Sulfur	Indicated on curve
MBT	1
Zinc stearate	6

companied by a degradation reaction which causes the cross-linking to go through a maximum and actually decrease during the later stages of cure. The specific effect of the MBT is to increase the rate of combination of the sulfur, with an accompanying increase in the amount of cross-linking which corresponds to that found in a nonaccelerated cure of the same combined sulfur level. This is shown in Table I. On the other hand, zinc in conjunction with MBT causes a large increase of the rate of formation of cross-links, with relatively little change in the rate of sulfur combination.

The effect of varying the concentration of sulfur, MBT, and zinc stearate, respectively, on cross-linking has also been determined. An increase of the concentration of sulfur, Figure 6, increased the ultimate amount of cross-linking in a regular fashion. However, the first proportion of sulfur produced a larger increment in the cross-linking than did succeeding amounts. These curves definitely show that degradation of the vulcanizates occurs simultaneously with the cross-linking. Thus, the measured amount of cross-linking is the resultant of the two reactions. Likewise, as the concentration of zinc stearate was increased in the proportions used in compounds of Figure 7, the ultimate amount of cross-linking became greater—in a manner similar to the results observed in the case of increased sulfur concentration. It is of particular interest that these vulcanizates exhibited a delayed curing action. Increasing concentrations of zinc stearate prolong the induction period, so that in the

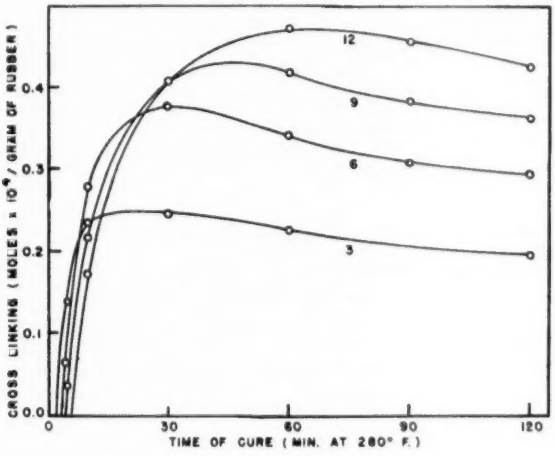


FIG. 7.—Effect of zinc stearate content on cross-linking.

Composition, parts per 100 parts rubber	
Sulfur	2
MBT	1
Zinc stearate	Indicated on curve

early part of the reaction those vulcanizates which contain the least amount of zinc stearate have the highest amount of cross-linking. Thus, the zinc stearate must participate in a reaction, probably with the MBT or sulfur, before the cross-linking reaction is initiated. The effect of the concentration of MBT on the cross-linking is shown in Figure 8. Although the rate of formation of cross-links was accelerated by increasing the concentration of MBT, the degradation reaction was also accelerated so that the ultimate amount of cross-linking is independent of the MBT concentration. Thus, MBT merely functions as a catalyst in the cross-linking reaction, probably by accelerating the sulfur-rubber combination reaction. It can, then, be concluded from the data presented in these three figures that the ultimate amount of cross-linking obtained in these gum stocks depends only on the concentration of sulfur and zinc and not on the MBT concentration, since the ultimate cross-linking is the resultant of the cross-linking and degradation reactions.

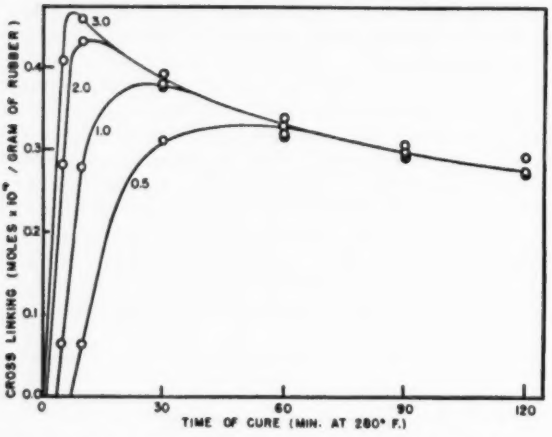


FIG. 8.—Effect of mercaptobenzothiazole concentration on cross-linking.

Composition, parts per 100 parts rubber

Sulfur	2
MBT	Indicated on curve
Zinc stearate	6

CROSS-LINKING AND ZINC SULFIDE PRODUCED

Several investigators[19] have advanced the theory that the vulcanization of natural rubber proceeds through the formation of thiol groups, which are produced in the rubber-sulfur combination reaction. These thiol groups then react with the soluble zinc present to form a zinc mercaptide cross-link. In the presence of free sulfur the zinc mercaptide is oxidized to a disulfide cross-link and zinc sulfide. Thus, for each mole of cross-linking in the vulcanizate, there

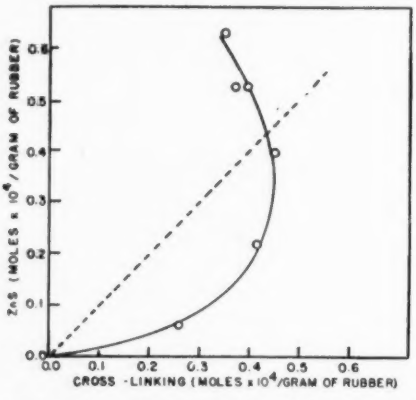


FIG. 9.—Comparison of amount of zinc sulfide and cross-linking.

Composition, parts per 100 parts rubber

Sulfur	2
MBT	1
Stearic acid	2
Zinc oxide	1

should be a mole of zinc sulfide formed. To test the veracity of this view, the zinc sulfide content of the vulcanizates was determined in addition to the amount of cross-linking. If a comparison is made between the data obtained from these two measurements, a general behavior common to all of the vulcanizates studied can be observed. This is illustrated in Figure 9 for a typical vulcanizate. At the beginning of the reaction, the cross-linking exceeds the amount of zinc sulfide, but the situation gradually reverses itself until, at long times of cure, the concentration of zinc sulfide is nearly double that of the cross-linking. A one-to-one correspondence represented by the dotted line is certainly not followed. It is true that if the cross-linking data were corrected for the amount of degradation that had occurred, a correspondence might be

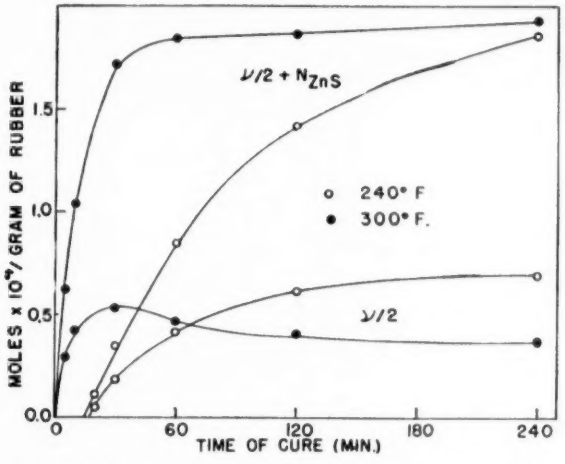


FIG. 10.—Effect of temperature of cure on cross-linking of natural rubber.

Composition, parts per 100 parts rubber	
Sulfur	2
MBT	1
Zinc oxide	2
Stearic acid	3.5

obtained in the later stages of cure. However, in the early stages, the cross-linking already exceeds the amount of zinc sulfide formed, so a correction for degradation would not improve the situation. It was thus concluded that the amount of zinc sulfide produced could not be correlated with the cross-linking in this manner.

On the other hand, it was observed that late, in the vulcanization reaction, the rate of formation of zinc sulfide was qualitatively equal to the rate of scission of the network due to degradation. In other words, during the period when almost all of the sulfur had reacted, the decrease in the cross-linking balanced the increase in zinc sulfide so that the sum of the two remained constant. This suggested that the zinc sulfide produced is a measure of the degradation that has occurred. In lieu of a better explanation of the data, it was assumed that for each mole of cross-linking destroyed one mole of zinc sulfide was formed.

Figure 10 illustrates graphically this relationship between the measured cross-linking, $\nu/2$, the amount of zinc sulfide, n_{ZnS}, and the sum, $\nu/2 + n_{ZnS}$,

for a natural-rubber gum stock cured at 240° and 300° F. The curves showing the change in $(\nu/2 + n_{ZnS})$ for the two temperatures of cure increase smoothly with time of cure to the same value. This is in contrast to the curves for the experimentally determined cross-linking, where the cross-linking of the vulcanizate cured at 300° F actually goes through a maximum and decreases to a value lower than that for the vulcanizate prepared at 240° F. The difference between the two sets of curves represents the amount of zinc sulfide produced. If the assumption that was made is true, it is also equal to the number of cross-links that are broken in the degradation reaction. The higher temperature of cure produces a larger amount of zinc sulfide, which would be expected since the higher temperature would favor degradation. Yet the sum approaches the same value for the two temperatures. Thus, this sum of the measured cross-linking and zinc sulfide will be taken equal to the true amount of cross-linking

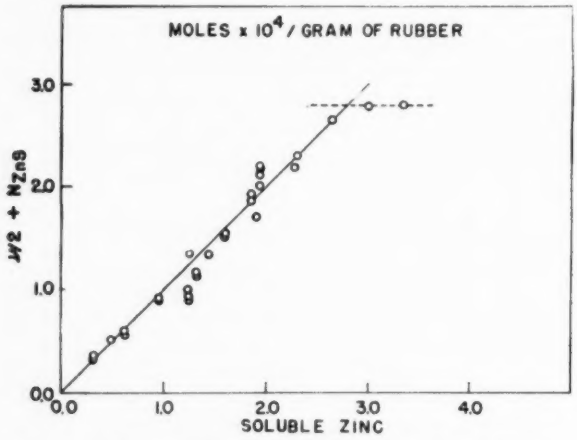


FIG. 11.—Effect of soluble zinc concentration on original cross-linking.

Composition, parts per 100 parts rubber	
Sulfur	2
MBT	1

formed (cross-linking in the absence of degradation). It will be called the original cross-linking.

Actually, little is known about the degradation reaction. The formation of zinc sulfide as one of the products of the degradation could be due to presence of hydrogen sulfide[18]. The hydrogen sulfide would then have to originate at, or react with, the cross-link if the amount of zinc sulfide is to be related quantitatively with the number of cross-links that are broken. This would imply, then, that the degradation occurs by rupture of sulfur bonds rather than chain scission.

The vulcanizates, for which the cross-linking data are shown in Figure 10, contain 2 parts zinc oxide per 100 parts rubber and 3.5 parts stearic acid per 100 parts rubber. It is estimated that this amount of stearic acid plus the naturally occurring acids will solubilize $1.85 + 10^{-4}$ moles of zinc per gram of rubber. The amount of soluble zinc in all the vulcanizates containing zinc oxide and stearic acid was taken equal to 1.23×10^{-4} moles plus one-half of the number of

moles of stearic acid present. It had been previously determined that the naturally occurring fatty acids in the rubber solubilized approximately 1.23×10^{-4} moles of zinc oxide per gram of rubber. This corresponds to approximately 1 part zinc oxide per 100 parts rubber. The ultimate amount of original cross-linking (1.95×10^{-4} moles per gram of rubber) obtained by the two curves in Figure 10 corresponds very closely to the amount of soluble zinc (1.85×10^{-4} moles per gram of rubber) present in the vulcanizate.

In Figure 11, the ultimate amount of original cross-linking is plotted as a function of the amount of soluble zinc for a series of vulcanizates. All the vulcanizates contained 2 parts of sulfur and 1 part of MBT per 100 parts rubber. Some of the vulcanizates contained zinc already in the soluble form, such as zinc

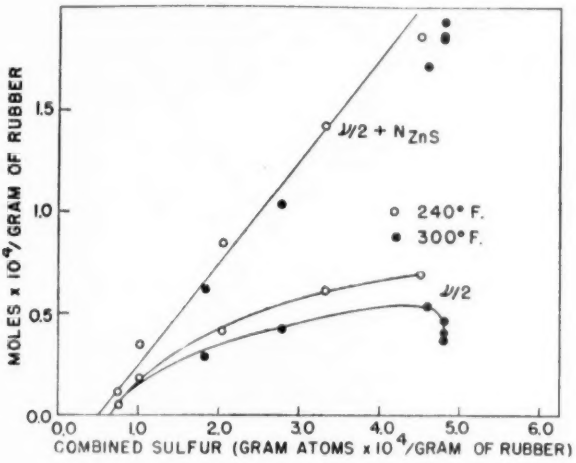


FIG. 12.—Relationship between cross-linking and combined sulfur.

Composition, parts per 100 parts rubber

Sulfur	2
MBT	1
Zinc oxide	2
Stearic acid	3.5

stearate, zinc propionate, and zinc benzoate; the others contained different amounts of zinc oxide and stearic acid. The amount of soluble zinc in these latter vulcanizates was estimated as previously explained. The straight line in Figure 11 represents a one-to-one correspondence between the moles of zinc solubilized and the ultimate original cross-linking. The experimental points scatter around this line fairly well. For each zinc atom added, a cross-link is formed which shows that zinc is involved in the stoichiometry of the cross-linking reaction. The most logical mechanism to explain this action would be the formation of zinc mercaptide cross-links from two thiol groups attached to different rubber molecules. However, it is possible to extract nearly all of the zinc from the vulcanizates with chloroform at any stage of the vulcanization reaction. The zinc was originally added as zinc stearate. Thus, the presence of any appreciable concentration of zinc mercaptide is unlikely.

CROSS-LINKING AND COMBINED SULFUR

If the original cross-linking, $\nu/2 + n_{ZnS}$, is plotted as a function of the amount of combined sulfur for the same two vulcanizates represented in Figure 10, the straight line of Figure 12 is obtained. The experimental points for either temperature of cure seem to fall on the same straight line. The slope of this line corresponds to the combination of two sulfur atoms with the rubber for each cross-link formed. If the sulfur combination reaction is the rate-determining step, then each cross-link is composed of two sulfur atoms. In the case of the experimentally determined cross-linking data, which is also included for comparison, the curves are lower and deviate considerably from the straight

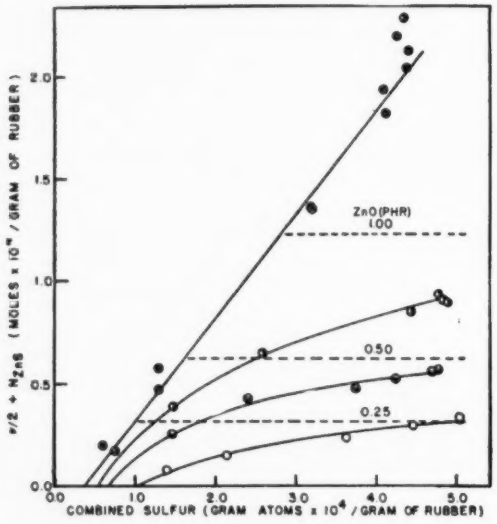


FIG. 13.—Effect of zinc concentration on utilization of sulfur for cross-linking.

	Composition, parts per 100 parts rubber			
	Stearic acid	Zinc oxide	Sulfur	MBT
○	0	0.25	2	1
◐	0	0.50	2	1
◑	0	1.00	2	1
●	4	6.0	2	1
⊕	6	6.0	2	1

line. The difference, of course, is due to the amount of degradation that occurs during the cure. This degradation produces sulfur which is still combined with the rubber but is not involved in the cross-linking. Thiol groups[20] are probably produced by this reaction in addition to zinc sulfide.

None of the curves of Figure 12 go through the origin, but all intercept the combined sulfur axis at some definite value. This value is fairly constant for all of the vulcanizates studied, and represents the amount of sulfur just necessary to produce a measurable amount of cross-linking. This is a function of the molecular weight of the rubber, as shown by Yanko[21] in his study of GR-S fractions. He found that the low molecular-weight fractions take more sulfur

than the higher fractions to obtain a measurable cure. However, the intercept found in the case of natural rubber represents a much larger amount of sulfur than would be necessary to join all of the molecules together with disulfide cross-links. The combined sulfur data have not been corrected for the original sulfur content of the pale crepe.

If the cross-linking is produced by a reaction of the zinc with sulfur attached to the rubber, then a plot of the cross-linking and combined sulfur will indicate the utilization of the sulfur for cross-linking. This is illustrated in Figure 13, which contains the data for natural rubber vulcanized with different levels of soluble zinc. At low levels of zinc the amount of combined sulfur exceeds that utilized in the cross-linking reaction. Consequently, the cross-linking falls

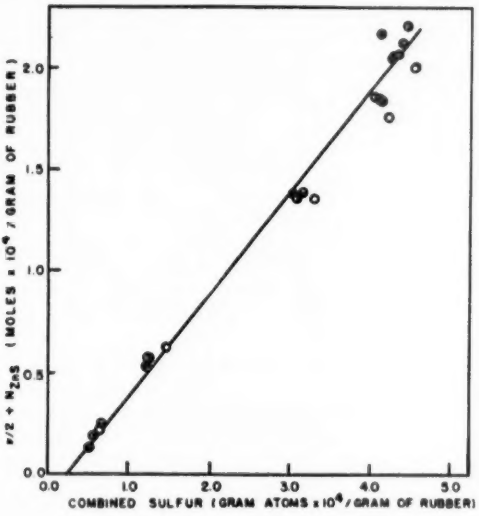


FIG. 14.—Cross-linking as a function of combined sulfur.

Composition, parts per 100 parts rubber	
Sulfur	2
MBT	1
Stearic acid	4
Zinc oxide ○	3
◒	6
◑	9
●	12

below the ultimate amount of one cross-link for every two sulfur atoms combined. The remaining combined sulfur is involved in other reactions, such as cyclization, that do not produce cross-links. However, the ultimate original cross-linking is still approximately equal to the total amount of soluble zinc contained in the vulcanizate. Only when the concentration of zinc is comparable to the total amount of combined sulfur that the linear relationship is followed. The behavior indicates that the minimum number of sulfur atoms involved in a cross-link is two. This is also shown in Figure 10. Here the maximum amount of original cross-linking obtained as the concentration of the zinc was increased was 2.8×10^{-4} moles per gram of rubber. Since these vulcanizates contained 2 parts of sulfur per 100 parts rubber (6.25×10^{-4} atoms per gram of rubber), this would correspond to 2.2 sulfur atoms per cross-link.

Thus, for a definite sulfur concentration, the efficiency of utilization of sulfur for cross-linking is determined by the concentration of soluble zinc. At low levels of zinc, poor efficiencies result, chiefly because part of the sulfur is never involved in cross-linking. As the concentration of zinc is increased, a point of maximum efficiency is reached corresponding to two sulfur atoms per cross-link. Yet the efficiency will never reach 100 per cent because of degradation. To obtain higher efficiencies, lower curing temperatures or other curing systems must be used. If TMTD is used as a curing agent, efficiencies approaching 100 per cent are obtained. The amount of zinc sulfide produced in a TMTD

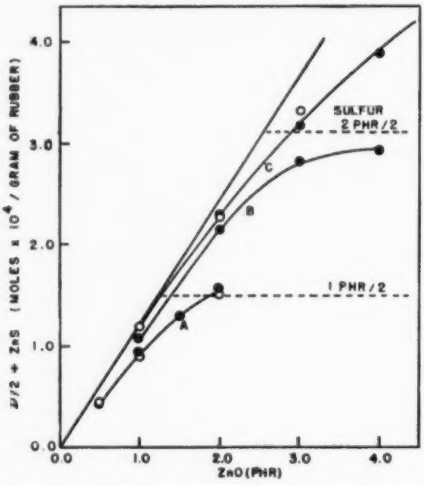


FIG. 15.—Effect of mercaptobenzothiazole on stoichiometry of cross-linking reaction.

	Composition, parts per 100 parts rubber	
	MBT	Sulfur
○	2	
●	1	
A		1
B		2
C		3

cure is negligible, in agreement with the original assumption of the degradation of cross-links to produce zinc sulfide.

In Figure 14 the original cross-linking is plotted as a function of the amount of combined sulfur for a series of vulcanizates containing various concentrations of zinc oxide. Again, the data correspond closely to a ratio of two sulfur atoms combining for each cross-link formed, represented by the straight line. These data also show that any zinc in excess of the fatty acid present has no effect on the vulcanization reaction. The amount of stearic acid added, 4 parts per 100 parts rubber, plus the natural fatty acid already present, is not sufficient to dissolve the lowest concentration of zinc oxide, 3 parts per 100 parts rubber; hence the higher concentrations of zinc oxide produce no effect on the cross-linking. It is only the proportion of soluble zinc present that influences the amount of cross-linking obtained.

The over-all effect of the three necessary compounding ingredients, sulfur, soluble zinc, and MBT, on the stoichiometry of the cross-linking reaction is shown in Figure 15. Stearic acid (10 to 8 parts) was added to all the vulcanizates; the amounts of the other compounds were varied. This is sufficient acid to solubilize approximately 3 parts zinc oxide per 100 parts rubber. The ultimate amount of original cross-linking is plotted against the amount of zinc oxide added to the vulcanizates. The data for the different sulfur levels fall fairly close to the straight line which represents a cross-link formed for each zinc atom added. In addition, the maximum amount of original cross-linking that can be obtained at the different sulfur concentrations by increasing the zinc concentration is approximately equal to one-half the sulfur concentration which corresponds to two sulfur atoms per cross-link. These relationships are independent of the MBT concentration, which apparently has no effect on the ultimate amount of cross-linking obtained.

It is realized that the type of evidence presented in this paper does not prove in a quantitative sense the original assumption that the amount of zinc sulfide produced is a measure of the degradation. Nevertheless, if this assumption is taken as a working hypothesis, several interesting relationships become apparent, namely, that the resultant cross-linking depends on the concentration of both the sulfur and soluble zinc. One atom of zinc and two atoms of sulfur produce one cross-link. However, the experimentally determined cross-linking is considerably lower than the original cross-linking because of the degradation reaction. Hence, this degradation accounts for the poor efficiency in the utilization of sulfur for cross-linking in sulfur vulcanization, especially at high concentrations of soluble zinc.

ACKNOWLEDGMENT

The authors take pleasure in acknowledging the assistance of R. D. Wolfangel in the development of the apparatus used for the determination of inorganic sulfide in the vulcanizates, and wish to thank Carol Liebler, who performed much of the experimental work.

This investigation was carried out under the sponsorship of the Office of Synthetic Rubber, Reconstruction Finance Corporation, in connection with the Government synthetic rubber program.

NOMENCLATURE

μ = Huggins interaction constant
M_c = molecular weight between cross-links
v_r = volume fraction of rubber in the swollen vulcanizate
ν = effective number of cross-linked units per gram rubber
ρ_r = density of rubber
V_0 = molar volume of solvent
f = force of retraction
A_0 = cross-sectional area of the test-specimen
R = gas constant
T = absolute temperature
α = ratio of the stretched swollen length to the unstretched swollen length of the test-specimen
β = ratio of the swollen length to the unstretched unswollen length of the test-specimen

χ = constant of the tension equation, proportional to the cross-linking
Q = amount of swelling (cc. solvent imbibed per cc. rubber)
ρ_s = density of solvent
γ = ratio of the swollen weight to initial weight of the test-specimen
S = soluble fraction of the vulcanizate
F = fraction of rubber in the compounded stock
n_0 = number of cross-links per gram rubber
M_n = primary molecular weight
n_{ZnS} = amount of zinc sulfide produced

REFERENCES

[1] Flory and Rehner, *J. Chem. Phys.* **11**, 52 (1943).
[2] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).
[3] Flory, Rabjohn, and Shaffer, *J. Polymer Sci.* **4**, 225 (1949).
[4] Bardwell and Winkler, *India Rubber World* **118**, 509 (1948).
[5] Gee, *J. Polymer Sci.* **2**, 451 (1947).
[6] Zapp, *Ind. Eng. Chem.* **40**, 1508 (1948); Zapp, Decker, Dyroff, and Rayner, *J. Polymer Sci.* **6**, 331 (1951); Zapp and Ford, *J. Polymer Sci.* **9**, 97 (1952).
[7] Scott and Magat, *J. Polymer Sci.* **4**, 555 (1949).
[8] Zhukov and Simkhovich, *Kolloid. Zhur.* **1**, 11 (1935).
[9] Flory, *J. Chem. Phys.* **18**, 108 (1950).
[10] Wall, *J. Chem. Phys.* **10**, 485 (1942); Treloar, *Trans. Faraday Soc.* **39**, 36 (1943); Flory, *Chem. Revs.* **35**, 51 (1944).
[11] Gee, *Trans. Faraday Soc.* **42**, 585 (1946).
[12] Scott, *Trans. Inst. Rubber Ind.* **5**, 95 (1929).
[13] Huggins, *Ind. Eng. Chem.* **35**, 216 (1943).
[14] Kelly, *India Rubber World* **66**, 491 (1922).
[15] Stevens, *Analyst* **40**, 275 (1915).
[16] Guppy, *Trans. Inst. Rubber Ind.* **7**, 81 (1931).
[17] Luke, *Ind. Eng. Chem. Anal. Ed.* **15**, 602 (1943).
[18] Craig, Juve, Davidson, Semon, and Hay, *J. Polymer Sci.* **8**, 321 (1952).
[19] Armstrong, Little, and Doak, *Ind. Eng. Chem.* **36**, 628 (1944).
[20] Zapp and Ford, *J. Polymer Sci.* **9**, 97 (1952).
[21] Yanko, *J. Polymer Sci.* **3**, 576 (1948).

THERMAL DECOMPOSITION OF VULCANIZED STRUCTURES OF DEFORMED VULCANIZATES CONTAINING VARIOUS ACCELERATORS *

B. Dogadkin and Z. Tarasova

Scientific Research Institute of the Rubber Industry, Moscow, USSR

According to the hypotheses developed by the authors, vulcanized rubber is a system in which the molecular chains are united by local molecular and chemical bonds of varying intensity. The concentration, distribution, and strength of these bonds determine the principal physical and mechanical properties of the vulcanizates. Consequently the study of the structure of the vulcanizate is of primary practical value.

The explanation of the nature of the bonds in a vulcanizate by chemical methods is very difficult, mainly because of the impossibility of distinguishing the specific chemical groups which enter into the composition of the different molecular chains from those bonds between the chains which are responsible for the development of spatial structures. From this view point, the thermomechanical method described below, which is based on the study of stress relaxation at different temperatures, is of great significance. As was shown by Dogadkin and Reznikovskiĭ[1], the delayed stress relaxation in a vulcanizate at temperatures up to 70° C is caused by rupture of the local intermolecular bonds and the regrouping of the structural elements of the polymeric chains without destruction of the chemical bonds between them. Accordingly, after some time at these temperatures, a practically balanced stress is established, which depends on the number of the stronger bonds remaining. At temperatures above 70° C, rupture of the chemical bonds between the chains takes place; its speed increases with decrease of the energy activating the rupture of the given type of bond. Particularly in the case of sulfur vulcanizates, we can assume that the following types of bonds exist between the chains of the rubber: (1) —C—C—, which develop as a result of the polymerization processes; (2) —C—S—C— monosulfide; (3) —C—S—S—C— disulfide, and (4) —C—S_n—C— polysulfide, formed as a result of the direct participation of the vulcanizing agent, sulfur, in the process of joining of the molecular chains. The energy of these chains can be estimated as 62.7 kcal. per mole for C—C, 54.5 kcal. per mole for C—S, and 27.5 kcal. per mole for the —S—S bond[2].

Naturally, the heat stability of a vulcanizate will depend on which of the indicated types of bonds predominates.

For the solution of this problem, the authors and M. M. Reznikovskiĭ constructed a dynamometer which made possible a study of stress relaxation of specimens in an inert gas (nitrogen). The dynamometer utilized a cork float, the weight of which and the degree of deformation were measured by the depth it was submerged in mercury, which in turn was regulated by a siphon apparatus (Figure 1).

* Translated for Rubber Chemistry and Technology by Alan Davis from *Doklady Akademiĭ Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik*, Vol. 85, No. 5, pages 1069–72 (1952).

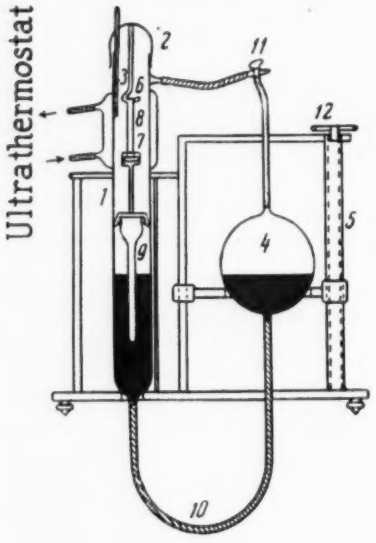


FIG. 1.—Diagram of floating dynamometer. 1. Thick-walled cylinder of molybdenum glass. 2. Ground-glass cover. 3. Thermometer. 4. Leveling bulb on a movable screw-rack (5). 6. Upper grip for ring-shaped specimen (8). 7. Lower grip for ring-shaped specimen (8). 9. Float with scale. 10. Thick-walled tubing. 11. Three-way stopcock for evacuation and filling of vessel with nitrogen. 12. Head of moving screw.

For the investigation, four types of vulcanized natural and butadiene-styrene rubbers were chosen: (1) with sulfur and without accelerator; (2) without sulfur, with tetramethylthiuramidsulfide as vulcanizing agent; (3) with sulfur and with diphenylguanadine as accelerator; and (4) with sulfur and mercaptobenzothiazole as accelerator. The composition of these vulcanizates insured a wide range of content of the types of bonds mentioned above.

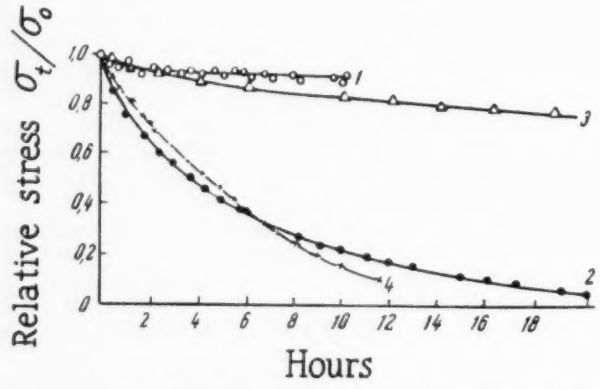


FIG. 2.—Relaxation of stress during heating in nitrogen. 1. All vulcanizates at 70° C. 2. Vulcanizate containing diphenylguanidine, at 100° C. 3. Vulcanizate containing thiuram, at 100° C. 4. Vulcanizate without accelerator, at 100° C.

The mixtures were prepared on a mill placed in a hermetic cabinet filled with nitrogen in order to eliminate any possibility of absorption of oxygen during mixing of the ingredients into the rubber. The ingredients were degassed, and the mixtures were vulcanized in a press in an atmosphere of nitrogen. Vulcanization was continued until all the vulcanizates, regardless of their composition, had practically the same moduli and swelling limits. In other words, all the vulcanizates had an identical concentration of chemical bonds between the molecular chains, equal to 7.0×10^{19} to 8.0×10^{19} bonds per cc.

Figure 2 shows the stress relaxation of vulcanizates of natural rubber at 70° C and 100° C after 100 per cent deformation. At 70° C, the decrease of stress takes place at the same rate in all the vulcanizates, since in this case relaxation is caused by destruction of the molecular forces which are roughly equal for all the vulcanizates (Figure 2, curve 1). At 100° C, a difference in the behavior of the vulcanizates was observed; those containing no accelerator or containing diphenylguanadine show a nearly complete loss of stress, and the irreversible part of the deformation is about 80 per cent. The vulcanizates containing thiuram disulfide relax up to 70 per cent of the original stress, and hardly any further stress is observed; the irreversible deformation is no more than 15 per cent of the original. The heat stability of the vulcanizates containing thiuram disulfide is evident at 130° C too; in this case, rupture of the specimens takes place before the stress relaxes to zero.

Thermal decomposition of the chemical bonds under stress follows a monomolecular mechanism. Assuming, according to contemporary theories of elasticity, that the stress is proportional to the number of nodes n, and that recombination of the free radicals, which form during the decay of the chemical bonds, takes place at the nodes, which have no stresses, we may write approximately:

$$\frac{d\sigma}{dt} = k_1 \frac{dn}{dt} = k' (n_0 - x)$$

After integration we have $\sigma_t = \sigma_0 e^{-k't}$, where σ_0 is the initial stress and σ_t is the stress at the moment of time t. In fact, as will be seen in Figure 4, at 130° C, $\log \frac{\sigma_t}{\sigma_0}$ in a wide range of observations is a linear function of the duration of relaxation. The kinetic constant of the stress relaxation process at 130° C for a vulcanizate without accelerator is $2.34 + 10^{-2}$, for one with diphenylguanidine, 8.05×10^{-3}, and for one with thiuram disulfide 1.035×10^{-3} min.$^{-1}$. The difference of stability of the bonds is also indicated by the fact that, with strict exclusion of oxygen, the vulcanizates without accelerator completely dissolve in a synthetic fuel solvent at 180–190° C, while those with thiuram do not dissolve when heated at 230° C for 60 hours.

On the basis of these results, one can conclude that vulcanizates with thiuram contain chiefly —C—S—C— monosulfide bonds and —C—C— bonds between the molecular chains of the rubber. This accords with the presumed mechanism of vulcanization by tetramethylthiuram disulfide, which in its decomposition evidently releases atomic sulfur, which in turn can form only —C—S—C— bonds, or else the disulfide is responsible for a radical mechanism of polymerization, with the formation of —C—C— bonds. Vulcanizates prepared with diphenylguanidine as accelerator or without any accelerator contain largely polysulfide bonds. The presence of these polysulfide bonds was established by extraction with acetone of the sulfur from vulcanizates by heating them in

a 10 per cent solution of sodium sulfite. The amount of sulfur extracted from the vulcanizates containing diphenylguanidine was 10–20 per cent of the total quantity of bound sulfur, while the vulcanizates containing thiuram contained no sulfur at all which could be extracted by sodium sulfite. The presence of polysulfide bonds in the vulcanizates obtained by heating rubber with elemental sulfur is evidently due to the fact that the initial step of vulcanization depends on the presence of an 8-member ring, S_8, which splits into radicals containing differing numbers of sulfur atoms, S_n. These polysulfide radicals bring about union of the molecular chains of the rubber.

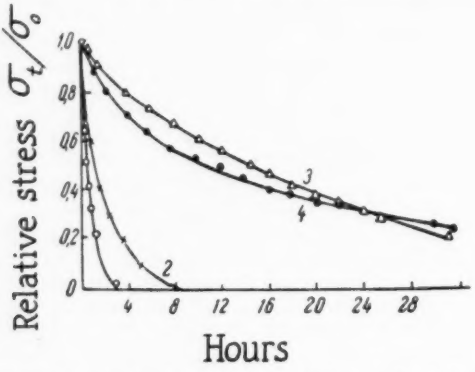


FIG. 3.—Stress relaxation during heating in nitrogen at 130° C. 1. Vulcanizate containing no accelerator. 2. Vulcanizate containing diphenylguanidine. 3. Vulcanizate containing tetramethylthiuram disulfide. 4. Vulcanizate containing mercaptobenzothiazole.

The type of rubber is of essential importance in determining the nature of the bonds in the vulcanizate; in particular, vulcanizates of butadiene-styrene rubber have a high heat stability, which would seem to be a consequence of the presence of a large number of —C—C— bonds in them, formed by the polymerization processes. The existence of these processes was established by the authors[3] from a study of the kinetic curves of the change of the modulus during vulcanization of butadiene-styrene rubber. As a result of the thermal decay of the intermolecular bonds in all vulcanizates of natural rubber, the swelling

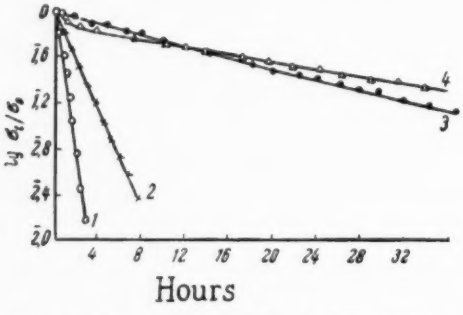


FIG. 4.—Stress relaxation as a function of time at 130° C. Curves correspond to those in Figure 3.

maximum in benzene is greatly increased; this attests to a decrease of the number of cross-links between the intermolecular chains in the rubber. Vulcanizates of butadiene-styrene rubber, with the exception of those obtained with thiuram as vulcanizing agent, show a decrease of the swelling maximum after heating under stress. This phenomenon is due directly to further combination of sulfur; analysis showed that the bound sulfur content in vulcanizates containing mercaptobenzothiazole after relaxation at 130° C increased from 2.0 to 3.73 per cent, and in vulcanizates without any accelerator from 1.72 to 3.25 per cent. In the case of the relaxation of vulcanizates extracted with acetone, the swelling maximum increased.

The structural changes of vulcanizates described in this work are of practical and theoretic interest in many aspects. First, they help to explain the basic cause of the thermal stability of vulcanizates. Purely thermal changes of the vulcanization structures unquestionably take place in the swelling processes, especially under the conditions of deformation of large rubber articles. Furthermore, in the light of this evidence of possibile thermal decomposition of vulcanization structures, it becomes necessary to extend our theories[4] about the causes of the phenomenon of a vulcanization optimum, inasmuch as, during vulcanization, the processes of decomposition of the sulfur structures must be taken into consideration, as well as the destructive effect of oxygen.

REFERENCES

[1] Dogadkin and Reznikovskiĭ, *Kolloid. Zhur.* **12**, 314 (1950).
[2] The energy of the —S—S— bond can be estimated in a different way as a dependency of the shape of the groups united with the S atoms. We used Eyring's data for polysulfide compounds.
[3] Dogadkin, Bartenev, and Novikov, *Kolloid. Zhur.* **10**, 94 (1948).
[4] Dogadkin, "Study of the Physics and Chemistry of Rubbers", **1950**, p. 21.

THE VISCOMETRIC DETECTION OF BRANCHING IN POLYMERS. I. BRANCHING IN GR–S AS A FUNCTION OF CONVERSION *

L. H. Cragg and A. T. Brown

Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario

INTRODUCTION

It is common practice to classify fractions of diene polymers as sol or gel, the sol fractions being those that dissolve in a variety of suitable solvents and the gel fractions those that do not dissolve, but only swell to a greater or lesser degree in these solvents. It is usually assumed that gel owes its insolubility to its three-dimensional netted structure and that, in contrast, the molecules in the sol fractions are linear. Indeed the term linear polymers, as commonly used, includes not only the unbranched-chain polymers but all polymers that are soluble in this sense[1]. It is now recognized, however, that the formation of branched molecules is possible in any addition polymerization. With simple vinyl monomers, like styrene, it can occur by chain transfer (a free-radical dehydrogenation of a growing or "dead" polymer molecule), and with dienes like butadiene it can occur both by this branching reaction and by the cross-linking reaction (a free-radical attack on a double bond either in the polymer chain or in a side vinyl group[2]. Although the branching reaction should yield soluble species (even when the molecular weight and extent of branching are high) the cross-linking reaction must lead eventually to an "infinite", and therefore insoluble, polymer network—the gel fraction. The formation of insoluble gel at high conversions is, of course, all too familiar in diene polymerizations. Often, for example in the preparation of synthetic rubber, it is considered desirable to stop such a reaction before the gel point is reached. The polymer so formed is soluble, but its molecules are not necessarily all linear. Indeed, it is to be expected from theory[2] that branched species are formed at all stages of the reaction and that the extent of branching increases with increasing conversion[3]. It is to be expected also that the presence of branched species would affect the physical properties of the polymer. Unfortunately, for lack of a suitable method of detecting branching and estimating its extent, it has not been possible to test these predictions directly or to determine to what extent an improvement of the physical properties of a polymer is due to increased branching and to what extent to other factors[4].

The Huggins constant k' has recently been shown[5] to be a fairly sensitive indicator of branching in chain polymers[6]. It seemed logical, therefore, to use it to study the factors that affect branching in a polymer. In the work reported in this paper, branching was studied as a function of conversion. A second paper[7] will be concerned with the effect of the temperature of polymerization.

* Reprinted from the *Canadian Journal of Chemistry*, Vol. 30, No. 12, pages 1033–1043, December 1952. This paper was presented at the Canadian High Polymer Forum, Annual Conference of the Chemical Institute of Canada, Ottawa, Ontario, June 1950.

In these experiments, samples of GR-S, prepared to four different conversions below the gel point, were carefully fractionated, and the value of k' for each fraction was determined by suitable viscosity measurements. Details of the experiments, and the conclusions drawn from them, follow.

EXPERIMENTAL

MATERIALS

Polymer

The polymer was prepared by emulsion polymerization at 119° F, using the mutual recipe, in the continuous reactor system at the plant of Polymer Corporation Ltd., Sarnia, Ont. Four samples were removed at different points, the conversions being 32.0, 45.1, 61.2, and 73.4 per cent, respectively. Each sample was stabilized with 1.25 parts of the antioxidant, BLE; then the unreacted monomers were removed by passing low-pressure steam through the latex for about 30 minutes, and the rubber was coagulated by the addition of sodium chloride solution and sulfuric acid. The rubber was dried under vacuum at room temperature. These very gentle conditions were found necessary to avoid changes in the polymer samples during drying, especially in those prepared to the two lowest conversions.

Solvents

Benzene.—Steel Company of Canada, ASTM industrial grade. Redistilled and dried and stored over sodium. $n_D^{25} = 1.4971$.

Methanol.—Carbide and Carbon Chemical Company, dried over calcium oxide. (Redistillation effected no change in refractive index.) $n_D^{25} = 1.3269$.

Phenyl-beta-naphthylamine (PBNA), obtained from Polymer Corporation, was added to fractions as a solution in benzene (10 g. per 100 cc. solution).

Precipitant.—A solution of equal volumes of the benzene and methanol described above. One large batch was prepared and was used for all fractionations. $n_D^{25} = 1.4102$.

PROCEDURES

Fractionation

Each of the polymer samples was fractionated by successive precipitation from solution in benzene (1 per cent by weight) using a 1 : 1 (by volume) solution of methanol and benzene as precipitant. The details of apparatus and technique are described elsewhere[8]. The only variations were that the original volume was 500 cc., the precipitation mixture was always allowed to stand 48 hours after cooling to 25° C, and the volume of PBNA solution added to the coacervate was 0.2 cc. Care was taken to keep the fractions small and fairly uniform in weight (most of them about 5–9 per cent of the whole). They were obtained as liquid coacervates, and were used without drying for the viscosity determinations. (Earlier experience had shown that, with GR-S, a careful primary fractionation such as this gave better results than could be obtained by refractionation of the primary fractions; with prolonged treatment changes in the fractions—particularly in those of highest molecular weight—were almost inevitable[7].

Viscometry

The viscometer was of the Ubbelohde type, modified to permit dilution in the bulb. It had been calibrated, and the very small kinetic-energy corrections

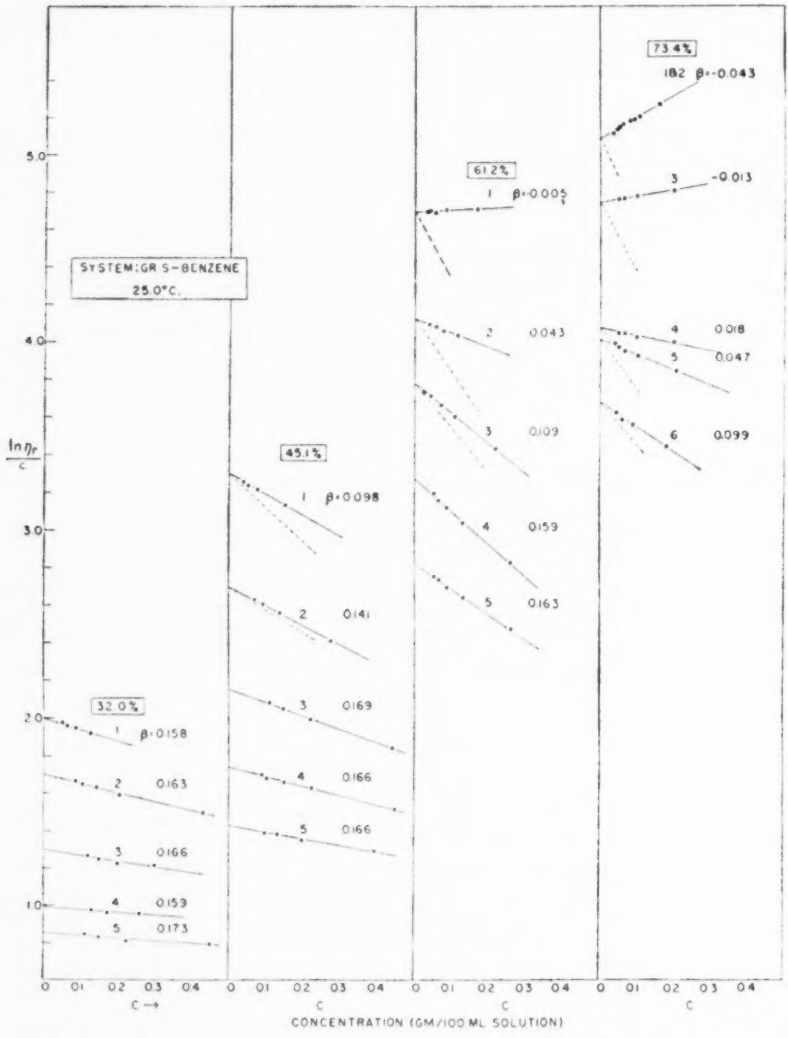


FIG. 1.—Inherent viscosity *vs.* concentration curves for the top fractions at four conversions.

were applied to all the data. Measurements were made at 25.0 ± 0.02° C, with the usual precautions[9], using four or five solutions of concentrations in the range 0.05 to 0.4 per cent (see Figure 1). Values of inherent viscosity $(\ln \eta_r)/c$ were computed and plotted against c, the concentration. The intrinsic viscos-

ity $[\eta]$ was obtained by linear extrapolation to $c = 0$. (Since concentrations were calculated in the units g. solute per 100 cc. solution, the units of intrinsic viscosity are dl. per g.) Because good straight lines were obtained, the equation of Mead and Fuoss[10]:

$$(\ln \eta_r)/c = [\eta] - \beta [\eta]^2 c$$

could be applied and the slope constant, β, calculated as—slope/$[\eta]^2$. From this constant β, the Huggins constant k' was calculated[11] from the equation: $k' = 0.50 - \beta$.

The concentration of the solution obtained by diluting the coacervate to 100 cc. was determined, in the manner described elsewhere[8], by careful evaporation of aliquot samples. The concentrations of the solutions used for viscometry measurements were calculated from the volume of this solution and of solvent used in preparing them, assuming no volume shrinkage on dilution.

RESULTS

Tables I, II, III, and IV record the experimental data: for each fractionation: W, the weight of whole polymer fractionated, W', the weight of rubber in

TABLE I

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 32.0% CONVERSION

(W = 5.32 g., W' = 4.47 g., C = 1.07 g. per 100 cc.)

Fraction	w(g.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.128	2.8_6	2.00	0.15_8	0.34_2
2	0.431	9.6_4	1.70	0.16_3	0.33_7
3	0.603	13.4_9	1.30	0.16_6	0.33_4
4	0.521	11.6_6	0.99	0.15_9	0.34_1
5	0.449	10.0_4	0.85	0.17_3	0.32_7

TABLE II

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 45.1% CONVERSION

(W = 5.30 g., W' = 4.74 g., C = 1.06 g. per 100 cc.)

Fraction	w(g.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.159	3.3_5	3.30	0.09_8	0.40_2
2	0.278	$.58_6$	2.70	0.14_1	0.35_9
3	0.442	9.3_2	2.17	0.16_9	0.33_1
4	0.449	9.4_7	1.74	0.16_6	0.33_4
5	0.394	8.3_1	1.43	0.16_6	0.33_4

TABLE III

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 61.2% CONVERSION

(W = 5.15 g., W' = 4.71 g., C = 1.04 g. per 100 cc.)

Fraction	w(g.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.168	3.5_7	4.69	-0.00_5	0.50_5
2	0.233	4.9_5	4.12	$+0.04_3$	0.45_7
3	0.218	4.6_3	3.78	0.10_9	0.39_1
4	0.259	5.5_0	3.27	0.15_9	0.34_1
5	0.262	5.5_6	2.82	0.16_3	0.33_7

TABLE IV

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 73.4% CONVERSION

(W = 5.08 g., W' = 4.71 g., C = 1.01 g. per 100 cc.)

Fraction	w(g.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.188	3.9_9	5.09	-0.04_3	0.54_3
2	0.321	6.8_2	5.09	-0.04_3	0.54_3
3	0.200	4.2_5	4.75	-0.01_3	0.51_3
4	0.203	4.3_1	4.08	$+0.01_8$	0.48_2
5	0.207	4.3_9	4.01	0.04_7	0.45_3
6	0.181	3.8_4	3.68	0.09_5	0.40_1

W (*i.e.*, the weight of material not extractable by the ethanol-toluene azeotrope[11], and C the concentration, in grams per 100 cc. of solution, of the solution before addition of precipitant; and for each fraction: w, the calculated weight of the dry fraction (this includes a negligible weight of antioxidant), w_x, the weight fraction ($= w/W'$), and the viscosity functions $[\eta]$, β, and k'. In Table V are the values of $[\eta]$, β, and k' for the whole samples.

TABLE V

INTRINSIC VISCOSITIES AND SLOPE CONSTANTS OF UNFRACTIONATED SAMPLES

Conversion	$[\eta]$	$[\eta]_{corr.}$	β	k'
32.0	0.75	0.89	0.16	0.34
45.1	1.13	1.26	0.16	0.34
61.2	1.68	1.84	0.14	0.36
73.4	2.17	2.34	0.08	0.42

In Figure 1 are drawn, for purposes of comparison, the $(\ln \eta_r)/c$ *vs.* c curves for all the fractions obtained. (Only the first five or six fractions were separated from each sample, as experience[8] had shown that branching, as indicated by high values of k', occurred principally in these fractions.)

DISCUSSION

Two effects of increasing conversion are clearly indicated by these results: as conversion is increased, both the molecular weight and the extent of branching are increased. As would be expected, these effects can be discerned most readily from the properties of the top fractions. Comparisons involving corresponding fractions of the four different samples should be meaningful because the fractionations were done in the same manner from solutions of the same initial concentration and the fractions were small (most of them 4–9 per cent of the whole sample).

BRANCHING

In earlier papers[13] it was shown that, for all of the fractions obtained from polystyrene (formed by emulsion polymerization at 55° C), the value of k' was the same, namely, 0.38 ± 0.02. When, however, a small proportion of divinylbenzene was copolymerized with the styrene, the fractions were not all alike in this respect; for the lower molecular weight ones the value of k' was the same as for the normal polystyrene, but for the higher ones, the value of k' increased with increasing molecular weight. This increase in k' was attributed to branching, and it was concluded that, when the degree of branching in a polymer was insufficient to cause gel, the branching occurred chiefly in the higher fractions.

Indeed, if the increase in k' above the base value (the normal value for linear polymer) was used as a measure, the degree of branching was too low to be detected in the lower fractions, but increased approximately linearly with molecular weight (intrinsic viscosity) in the higher fractions.

From the data of Tables I, II, III, and IV and Figure 1, it is clear that GR-S behaves in these respects much like lightly cross-linked polystyrene. From this and other evidence[14] the "base value" of k'—for which we shall use the symbol

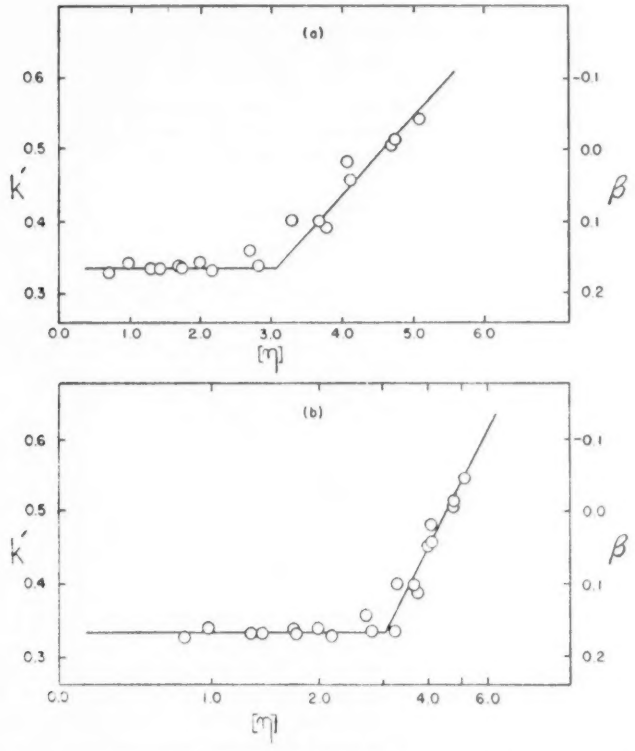


FIG. 2.—Relation between slope constants and intrinsic viscosity for all fractions studied (*a*) k' (and β) *vs.* $[\eta]$, (*b*) k' (and β) *vs.* log $[\eta]$.

k'—for poly(butadiene-co-styrene) of this composition is 0.33 ± 0.01, corresponding to a value of β of 0.17 ± 0.01. At 32.0 per cent conversion the first five fractions all have this value of β (and k'), hence are presumably branched very little or not at all. At 74.3 per cent conversion, on the other hand, none of the fractions has this value, and the discrepancy becomes more marked the higher the intrinsic viscosity. In Figure 1 this discrepancy is emphasized, when it occurs, by drawing a dotted line to indicate what the slope of the line would have been if the fraction had had the normal value of β (*i.e.*, -0.17).

We conclude, therefore, that with GR-S (1) the degree of branching increases markedly with conversion, (2) there is little or no branching in the

polymer formed at low conversion (30 per cent), and, (3) when branching does occur the species most affected are those of highest molecular weight.

This connection between molecular weight and branching deserves more attention. From our data it follows that polymer species formed in a polymerization of this type do not exhibit branching, at least not to a degree detectable by this method, unless the molecular weight exceeds a certain value. This is made clearer in Figure 2(*a*), in which k' for each fraction is plotted against intrinsic viscosity. Below $[\eta] \approx 3$ the values of k' are normal; above $[\eta] \approx 3$, k' starts to increase. (In Figure 2 (*b*), k' is plotted against log $[\eta]$ to emphasize the abruptness with which k' begins to increase.) One would expect on theoretical grounds that branching would take place all through the polymerization and that short molecules as well as long ones would be affected, though not as many of them, nor to as high a degree. However, during the early stages of the reaction, when the thiol concentration is high, neither the polymer molecules nor any branches formed on them can grow long. The relatively few

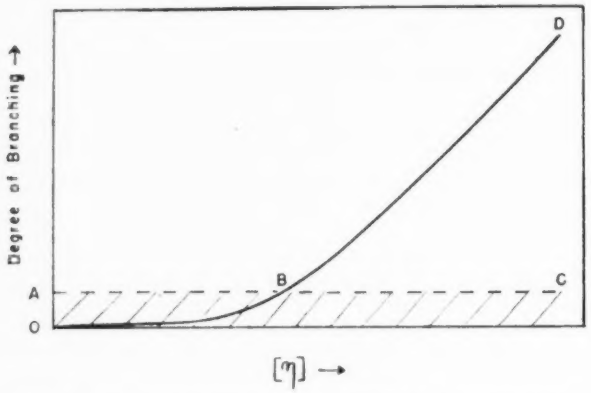


FIG. 3.—Hypothetical variation of degree of branching with intrinsic viscosity.

branched molecules would have only one or two short branches, hence would differ little in their viscosity behavior from unbranched molecules. Later in the polymerization, when the thiol concentration is lower, a branch started on one of these shorter molecules can grow longer, but then the resulting molecule will be a longer molecule more prone to further branching. (It must be remembered that the intrinsic viscosity of a fraction is an indication of the effective length of the finished molecules, not of the length of the molecules before any branching occurs.) The molecules that would differ appreciably in viscosity behavior (especially with respect to polymer-polymer and polymer-solvent interaction, which affects β and k') would be the "bushier" ones and these would be the ones of greater effective length. An increase of k' would not, therefore, be apparent at low molecular weights. If, for example, the degree of branching[15] were to increase with intrinsic viscosity, as indicated by the curved line *OBD* in Figure 3, and if the degree of branching had to be greater than *OA* to be detectable as an increase in k' (greater than the experimental error), then, assuming that thereafter the increase in k' is roughly proportional to the degree of branching, k' would be constant up to an intrinsic viscosity corresponding to

B and then would increase rapidly (*cf.* Figure 2). This would explain, too, why the points for the fraction from all four conversions fall approximately on the same curve. (The polymer molecules formed at all stages of the reaction up to 74 per cent conversion have approximately the same butadiene content[5] and, therefore, the same number of potential sites for attack per unit length. By contrast, increasing the content of divinylbenzene in poly(styrene-co-divinylbenzene) should increase the likelihood of attack on a given length of molecule, and hence cause detectable branching at lower molecular weights.

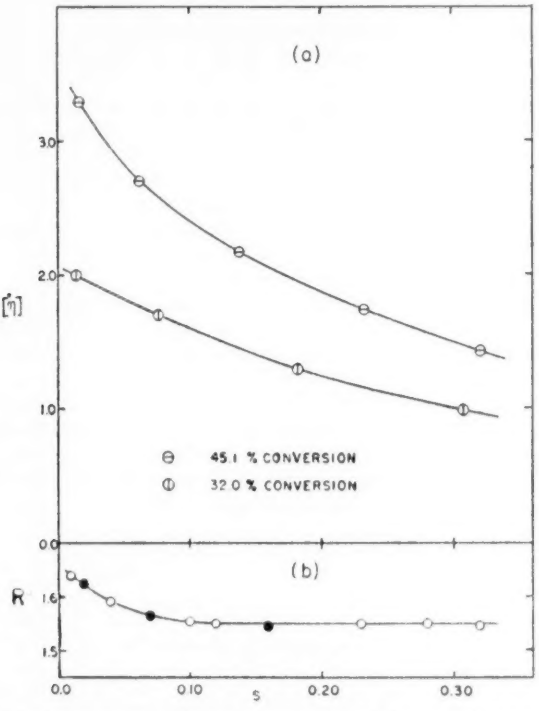


FIG. 4.—(*a*) Distribution curves for the two low-conversion samples: intrinsic viscosity *vs.* (corrected) cumulative weight fraction, *s*. (*b*) Intrinsic viscosity ratio, $R(=[\eta]_{45}/[\eta]_{32})$, *vs.* cumulative weight fraction, *s*.

This is indeed what is indicated by the data obtained with cross-linked polystyrene[16]. And if, as seems likely[17], branching in butadiene-styrene copolymers is due mainly to the cross-linking reaction, one would expect that, other things being equal, the degree of branching in such copolymers would decrease with increasing proportion of combined styrene.)

BRANCHING AND MOLECULAR WEIGHT

The familiar increase of average molecular weight as emulsion polymerization proceeds is evidenced both by the increase in intrinsic viscosity of the whole rubber (Table V) and by the similar increase for the corresponding fractions.

There are two principal reasons for this effect. First, as the reaction proceeds, the concentration of thiol decreases; hence a polymer molecule formed later has a better chance of growing large before its growth is terminated by an encounter with a thiol molecule; second, the longer the period of reaction the greater is the chance that a given molecule will be attacked by a radical and start growing a branch and the greater is the chance, therefore, that it will become larger. The effects of these two factors on the molecular-weight distribution would not be the same. The first should affect all molecular species in the same proportion; the second should affect most those that already have the highest molecular weight. In other words, one might expect the increase of molecular weight to be relatively the same for the comparable low fractions, but relatively higher for the top fraction or fractions in which branching is detectable.

Unfortunately a direct test of this prediction is not possible with these measurements because the corresponding fractions at different conversions are not strictly equal in weight. There is, however, sufficient similarity between the fractionations of the two low-conversion samples (32.0 and 45.1 per cent) to make possible an indirect test. In Figure 4(*a*) are plotted the integral molecular-weight distribution curves (as much of them as the data permit) for these two samples, s is a function (closely related to the cumulative weight fraction, q), whose value for the nth fraction is obtained by adding one-half the weight fraction of the nth fraction to the cumulative weight fraction for the $(n-1)$th fraction. From such a curve, one can obtain the intrinsic viscosity for the molecular species precipitating at any given cumulative weight[18] fraction, q.

The ratio $[\eta]_{45}/[\eta]_{32}$ (where $[\eta]_{45}$ refers to species from the 45.1 per cent conversion sample and $[\eta]_{32}$ to species taken, at the same cumulative weight fraction, from the 32.0 per cent conversion sample) is thus a measure of the relative molecular weights of the species. Assuming the relation $[\eta] = K M^{2/3}$, which is sufficiently accurate for present purposes:

$$[\eta]_{45}/[\eta]_{32} = (M_{45}/M_{32})^{2/3}$$

or

$$M_{45}/M_{32} = ([\eta]_{45}/[\eta]_{32})^{3/2} \qquad (1)$$

In Figure 4(*b*), values of $[\eta]_{45}/[\eta]_{32}$ are plotted against the values of s at which the intrinsic viscosities $[\eta]_{45}$ and $[\eta]_{32}$ are read from Figure 4(*a*). This ratio apparently has a constant value, 1.5$_0$, except in the region of highest molecular weight (below $s = 0.10$) where it increases with increasing molecular weight. Since detectable branching appears only in this region, and only in the 45 per cent–conversion fractions, this evidence is consistent with the suggestion that increase of molecular weight due to branching should be most apparent in the high molecular weight species, whereas the increase due to decrease in thiol concentration should be relatively the same for all species. (It might be objected that because the intrinsic viscosity—molecular weight relationship for branched species is different[19] from that for linear species, a change of the ratio $[\eta]_{45}/[\eta]_{32}$ does not necessarily mean a corresponding change of the ratio M_{45}/M_{32}. Since, however, the branching leads to a lower intrinsic viscosity for a given molecular weight, an unusually high value of the ratio $[\eta]_{45}/[\eta]_{32}$ is indicative of an even higher moecular-weight ratio than would be predicted from Equation (1). The argument, then, is strengthened rather than weakened.)

The curves of Figure 4(*a*) can also be used to estimate what would be the intrinsic viscosity of successive fractions of any specified size. Thus values at $s = 0.020$, 0.070, and 0.150 would be those of successive fractions of weight fractions 0.040, 0.060, and 0.120, respectively. (These points are chosen so that the hypothetical fractions at the two conversions correspond as closely as possible to the actual fractions obtained from the two samples.) Thus, if the fractionations had been done in such a way that the two first fractions had been exactly the same proportion of the whole (both 0.040), $[\eta]_{45}/[\eta]_{32}$ would have had the value 1.6_5. (The value for the two first fractions actually obtained—the only ones that were very close to being the same size proportionately—is, in fact, 1.6_5.) Similarly, for the second fractions—both 0.060—this ratio would have been 1.5_3, and for the third fractions 1.4_9. These three values are plotted, as filled circles, in Figure 4 (*b*). (The open circles represent values of $[\eta]_{45}/[\eta]_{32}$ calculated in a similar way for other values of s.) Assuming that a value of $[\eta]_{45}/[\eta]_{32}$ greater than 1.5_0 is due to branching, and that branching is negligible in all fractions at 32 per cent conversion (see above), this means that, at 45 per cent conversion, there is appreciable branching in the first fraction, a slight suggestion of it in the second, and none (detectable) in the third and subsequent fractions. It is significant, or else a remarkable coincidence, that these are precisely the conclusions reached from the slope-constant measurements.

Too much should not be made of this evidence, of course, but it is at least promising enough to suggest that further evidence of a similar nature might be worth seeking. And it certainly is consistent with the conclusion, based on the sounder evidence from slope constants, that the effects of branching are noticeable only in the high molecular weight species.

Recently, after this work was completed and the paper presented, Johnson and Wolfanger[20] reported that the exponent a in the relationship $[\eta] = K M^a$ decreased as the conversion of emulsion polybutadiene increased from 20.5 to 81 per cent, and presented evidence to prove that this drop in the exponent was predominantly due to increasing degree of cross-linking (branching). Since polybutadiene and the copolymer of butadiene and styrene that we studied should behave similarly with respect to branching and cross-linking, their conclusions and ours are mutually supporting.

SUMMARY

Samples of GR-S were taken from a continuous emulsion-polymerization system at conversions 32.0, 45.1, 61.2, and 73.4 per cent, respectively, and each, after careful drying, was carefully fractionated to give five or six top fractions. For each of these fractions, values of intrinsic viscosity $[\eta]$ and of the viscosity slope constants, β and k', were determined. As with normal and cross-linked polystyrene, β and k' appear to be constant for all linear species, but to have higher values for branched species, the increase being a measure of the extent or degree of branching. From the data obtained it is concluded that in GR-S there is little or no branching at low conversions, that the degree of branching increases markedly with increasing conversion, and that branching occurs to the greatest degree in the species of highest molecular weight.

There seemed to be, for this polymer at least, a molecular weight below which branching could not be detected, regardless of conversion, but above which branching increased with increasing molecular weight.

ACKNOWLEDGMENTS

We are grateful to Polymer Corporation, Ltd., and to H. L. Williams, J. S. Tapp, and N. R. Legge for assistance of various kinds, and to the National Research Council of Canada for financial aid.

REFERENCES

[1] Frith and Tuckett, "Linear Polymers", Longmans, Green & Co., London, **1951**; Huggins *et al.*, *J. Polymer Sci.* **8**, 257 (1952).

[2] Flory, *J. Am. Chem. Soc.* **69**, 2893 (1947).

[3] The branching reaction and cross-linking reaction both yield branched molecules. When polymerization proceeds beyond the gel point, the former gives a product easily distinguishable from the latter. At lower conversions, however, the branched species formed by the two mechanisms are indistinguishable in their viscosity behavior. See Walker and Winkler, *Can. J. Research* **B28**, 298 (1950).

[4] Gehman, *Ind. Eng. Chem.* **44**, 730 (1952).

[5] Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1942).

[6] Walker, and Winkler, *Can. J. Research* **B28**, 298 (1950); Cragg, and Manson, *J. Polymer Sci.* **9**, 265 (1952); Manson and Cragg, *Can. J. Chem.* **30**, 482 (1952).

[7] Cragg and Fern, Part II of this series; the following paper in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.

[8] Cragg and Switzer, paper presented at the Canadian High Polymer Forum, Hamilton, Ontario, June **1949**.

[9] Cragg, Rogers, and Henderson, *Can. J. Research* **B25**, 333 (1952).

[10] Mead and Fuoss, *J. Am. Chem. Soc.* **64**, 277 (1942).

[11] Ewart, in "Advances in Colloid Science", edited by Mark and Whitby, Interscience Publishers, Inc., New York. **1946**. Vol. 2. The constant β was determined instead of k' for reasons already cited (see Manson and Cragg, *Can. J. Chem.* **30**, 482 (1952)). Nevertheless, k' is calculated and used in the discussions because it is the more familiar constant. It should be clearly understood, however, that the values of k' are calculated, not measured; the true value of k' will not be precisely the same as our calculated value because the equation used is probably not strictly valid at finite concentrations. The error will, however, be small and constant, and, particularly since we are interested in differences in k', will not affect the conclusions.

[12] Fuller, *Bell System Tech. J.* **25**, 351 (1946).

[13] Manson and Cragg, *Can. J. Chem.* **30**, 482 (1952); Cragg and Manson, *J. Polymer Sci.* **9**, 265 (1952).

[14] Cragg and Fern, Part II of this series; the following paper in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.

[15] It is, and probably will continue to be, impossible to define "degree of branching" precisely in terms of structure, for branched molecules can differ in the length of the primary chain and in the length, complexity, and density (number per unit length of primary chain) of branches. Very short branches on a long primary chain will have little effect on viscosity behavior, but considerable effect on crystallizability. Hence "degree of branching" has quantitative meaning, only in respect to a measurable effect on some specified physical property. As we use the term, the degree of branching increases when the changes in branching are such as to cause an increase in the effect on viscosity behavior (specifically, an increase in k'–k').

[16] Cragg and Manson, *J. Polymer Sci.* **9**, 265 (1952).

[17] Sivertz, C. S. Unpublished results, University of Western Ontario, London, Ont. **1951**.

[18] For infinitesimal fractions the cumulative fraction:

$$q(=\sum_{i=1}^{n}(w_x)_i)$$

has for all practical purposes the same value as

$$s(=\sum_{i=1}^{n-1}(w_x)_i+0.5\,(w_x)_n)$$

[19] Johnson and Wolfangel, *Ind. Eng. Chem.* **44**, 752 (1952); Thurmond and Zimm, *J. Polymer Sci.* **8**, 477 (1952).

[20] Johnson and Wolfangel, *Ind. Eng. Chem.* **44**, 752 (1952).

VISCOMETRIC DETECTION OF BRANCHING IN POLYMERS. II. BRANCHING IN POLY(BUTADIENE-CO-STYRENE) AS A FUNCTION OF POLYMERIZATION TEMPERATURE *

L. H. Cragg and G. R. H. Fern

Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario

INTRODUCTION

Previous experience with polystyrene, normal and cross-linked[1], and with GR-S[2], gave strong support to our belief that, in careful viscosity measurement and evaluation of either of the slope constants[3] β and k', a useful and convenient means is available for the detection and measurement of branching in soluble high polymers. Moreover, since the measurements are made on separate fractions, information can be obtained regarding the relation between the size of polymer molecules and the degree to which they are branched.

In the work reported here, this method was applied in a study of the effect of the temperature of polymerization on branching. It is now well known, of course, that, by reducing the temperature of polymerization, desirable changes of the physical behavior of emulsion polymers may be effected. This observation led to the development of "cold rubber" as an improvement over GR-S for use in tire tread stocks. Many efforts have been made to explain this superiority on the basis of changes in molecular structure[4]. Several effects of lowering the temperature of polymerization have been noted: a narrowing of the molecular-weight distribution[5], a slight decrease of the proportion of the 1,2-isomer[6], a more marked increase of the proportion of the *trans*-form of the 1,4-isomer[7], and a decrease of the extent of chain branching. Of these various effects, the one most difficult to detect and to measure quantitatively is chain branching[8]. (The infrared technique so valuable with polythene[9] is unfortunately inapplicable to other addition polymers.) There is some convincing qualitative evidence of a decrease of branching: thus, at a comparable high conversion, less gel is formed at the lower temperatures; or—another manifestation of the same effect—in polymers formed from the same recipe, the gel point, as indicated by the peak in the vistex *vs.* conversion curves, occurs at higher conversions as the temperature of polymerization is lowered[10]. Again, the exponent a in the Mark-Houwink expression: $[\eta] = kM^a$, is higher for polybutadienes prepared at lower temperatures, an effect attributed to decreased branching because it was similar to those observed: (*a*) with decreased conversion at constant temperature[11], and (*b*) with decreased divinylbenzene content in copolymers of divinylbenzene and styrene[12]. The first of these methods, however, provides no measure of branching below the gel point, and the second is relatively insensitive and inconvenient (involving, as it does, either osmotic pressure or light-scattering measurements in addition to viscos-

* Reprinted from the *Journal of Polymer Science*, Vol. 10, No. 2, pages 185–199, February 1953. This paper was presented at the Canadian High Polymer Forum, Annual Conference of the Chemical Institute of Canada, Montreal, Quebec, June 1952.

ity measurements). There was still need, therefore, for measurements that might throw further light on the influence of temperature on branching. Accordingly, samples of rubber were prepared at 15, 30, 40, and 50° C, using a basic redox recipe with only such minor modifications as were required to yield samples of about the same intrinsic viscosity in about the same reaction time at about the same conversion. These were carefully fractionated; and values of $[\eta]$, β, and k' were determined for the fractions. The results indicate clearly that branching in these rubbers decreased steadily as the temperature of polymerization decreased, and became undetectable in the rubber prepared at 15° C.

EXPERIMENTAL

MATERIALS

Polymers.—The samples of rubber used in these experiments were prepared for us in the Research and Development Laboratories at Polymer Corporation Ltd., Sarnia. The polymerizations were conducted in emulsion, in 8-oz. bottles, revolving in water baths maintained at the desired temperature. The

TABLE I

DATA REGARDING THE POLYMER SAMPLES AND THEIR PREPARATION

(Weights are expressed as parts by weight)

	Polymerization temperature				
	50° C		40° C	30° C	15° C
Polymer code	RD 226	RD 261	RD 216	RD 225	RD 245
Fractionation code	FR 8	RF 13	RF 7	RF 9	RF 10
Conversion (%)	62.4	65.8	64.2	62.8	62.0
Reaction time (hr.)	18	16	15	15	18
ETA extract (%)	8.36	8.64	10.15	7.98	9.39
Butadiene	72	72	72	72	72
Styrene	28	28	28	28	28
Water	180	180	180	180	180
MTM-4[a]	0.32	0.39	0.32$_5$	0.32	0.28
Cumene hydroperoxide	0.10	0.10	—	0.10	—
p-Menthane hydroperoxide	—	—	0.12$_5$	—	050
Dresinate-214	4.7	4.7	4.7	3.0	4.7
KCl	0.5	0.5	0.5	0.5	0.5
Daxad-11	0.1	0.1	0.1	0.1	0.1
$FeSO_4 \cdot 7H_2O$	0.05	0.04	0.15	0.07	0.04
Sodium Kalex	0.10	0.10	0.10	—	—
DTBHQ[b]	0.30	0.30	0.30	0.30	0.30
Dextrose	—	—	—	1.00	—
KOH	—	—	—	0.13	—
$K_4P_2O_7$	—	—	—	0.089	—
Citric acid[c]	—	—	—	—	0.1

[a] Mixed tertiary thiols.
[b] Di-(*tert*-butyl) hydroquinone.
[c] The pH of the ferrous sulfate-citric acid activator was adjusted to 9 with sodium hydroxide.

recipes used at the various temperatures are shown in Table I; they are basically the same, the slight modifications having been made to obtain polymers of about the same intrinsic vistex (1.9 to 2.0) in about the same reaction time, at comparable conversions (about 65 per cent) well below the gel point. Samples large enough for fractionation were obtained by combining the latex from several bottles. Unreacted monomers were removed by "stripping" with low

pressure steam, and antioxidant (1.25 parts BLE) added. The rubber was separated by coagulation with sodium chloride solution and sulfuric acid, and dried very carefully (under vacuum at room temperature) to minimize further cross-linking. Every sample so prepared remained completely free of insoluble gel.

Solvents.—Benzene (Steel Company of Canada), ASTM Industrial Grade, fractionally distilled, dried and stored over sodium, and filtered through finely sintered glass, b.p. 80.0–80.5° C, n_D^{25} 1.49720. *Methanol* (Union Carbide and Carbon Chemical Co.), synthetic, redistilled, filtered, and stored in a ground-glass stoppered bottle; its refractive index, $n_D^{25} = 1.3269$, did not change throughout the period of use. *N-Phenyl-beta-naphthylamine* (PBNA), (obtained from Polymer Corporation) used as a solution in benzene (10 g./100 cc. solution). *Precipitant*, prepared by mixing exactly equal volumes of purified benzene and methanol; a fresh batch was prepared for each fractionation; $n_D^{25} = 1.4093 \pm 0.0001$.

PROCEDURES

Fractionation.—The method was essentially that described earlier[2], fractions being obtained in the form of liquid coacervates by step-wise addition of precipitant to a dilute solution of rubber in benzene. To avoid gelling of fractions due to prolonged handling, only a one-stage fractionation was attempted; to make this as efficient as possible the initial concentrations were kept low (about 1 per cent)[13], and all fractions were kept small; and to make comparisons between fractions of different samples as meaningful as possible, great care was taken—and it had to be great, especially for the first one or two fractions—to make all fractions of about the same weight (on a dry basis). As in the earlier work[14], fractionations were not completed, but were discontinued when the fractions no longer showed evidence of branching (*i.e.*, when β and k' for the fraction had reached the constant value characteristic of unbranched species).

Viscometry.—The viscometer used was of the Ubbelohde type, specially modified to permit dilution of the solution while in the viscometer[15]. It is designed to have negligible kinetic energy effects, and careful calibration showed that indeed the kinetic energy correction was much less than the experimental error. Measurements were made at 25.00 ± 0.02° C. The usual precautions were taken in loading the viscometer, in obtaining and maintaining thermal equilibrium, and in measuring flow times[16]. Values of inherent viscosity were calculated and plotted against concentration; $[\eta]$ was obtained by linear extrapolation (see Figure 1) as $\lim_{c \to 0} (\ln \eta_r)/c$, and β was calculated from the slope of the line: ($\beta = -$ slope$/[\eta]^2$). The Huggins slope constant k' was, in turn, obtained from β, using the relation[17]:

$$k' = 0.50 - \beta$$

Although special care was taken with the successive dilutions of the solution in the viscometer (measuring all volumes with the same calibrated pipette, refiltering the benzene through finely sintered glass, mixing the solutions thoroughly after dilution), points were occasionally obtained such that it was difficult to decide where to draw the best line. In such instances the viscometer was carefully cleaned and the whole determination repeated. With patience and practice, it was possible to reduce considerably the uncertainty of the slope of the inherent viscosity-concentration lines and, therefore of β and k'.

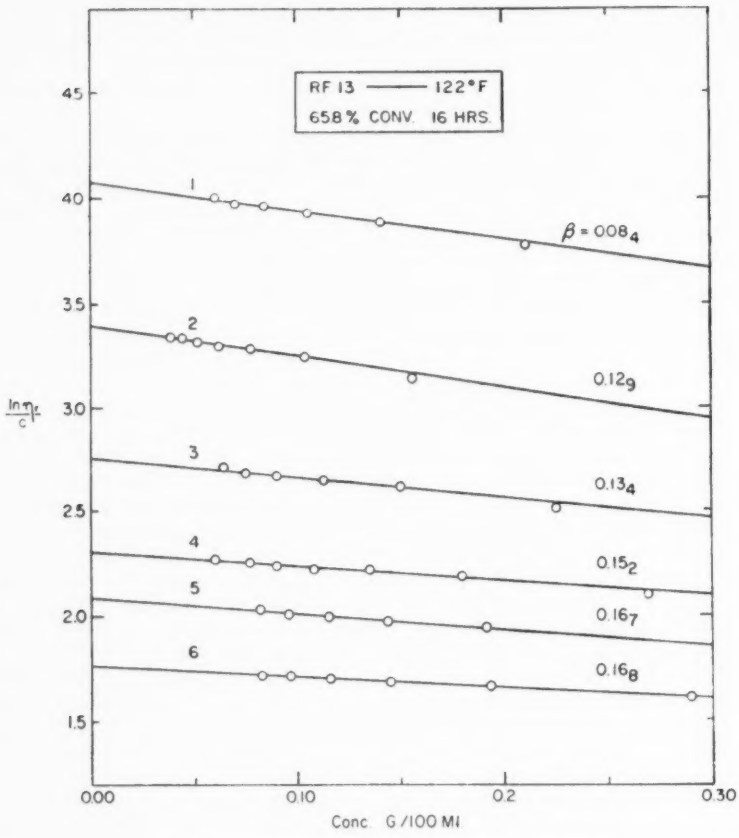


FIG. 1.—Representative plots of inherent viscosity *vs.* concentration.

TABLE II

DATA FOR FRACTIONS OF RUBBER POLYMERIZED AT 50° C (RF-8)

W = 5.67 g. C = 1.136 g./100 cc. W' = 5.19 g.

Fraction	w(g.)	$\frac{w_x}{W}$ (×10²)	$[\eta]$	β	k'
1	0.2014	3.88	4.72_1	0.04_9	0.46_1
2	0.1889	3.64	3.60_4	0.10_8	0.39_2
3	0.2492	4.80	2.96_0	0.14_0	0.36_0
4	0.3176	6.11	2.58_6	0.13_4	0.36_4
5	0.3325	6.40	2.29_7	0.16_0	0.34_0
6	0.2289	4.40	1.95_6	0.17_6	0.32_4
7	0.2625	4.05	1.75_0	0.17_9	0.32_1
8	0.1435	2.76	1.59_0	0.17_7	0.32_3
9	0.2029	3.90	1.43_0	0.18_6	0.31_4
10	0.1901	3.65	1.40_7	0.18_0	0.32_0

As before[13], the concentration of the most concentrated of each set of solutions was determined (in triplicate) by careful evaporation of weighed portions, and the concentrations of the others were calculated from this one assuming no volume shrinkage on dilution. (An error in the original concentration determination will affect the value of intrinsic viscosity but not that of β or k'.)

RESULTS

The essential data are in Tables II, III, IV, and V. For each fractionation are recorded the initial concentration, C, of solution (*i.e.*, before addition of any precipitant), the weight, W, of dry sample taken, and the weight, W', of polymer in this sample (or, more precisely, the weight of material after extraction by the ethanol-toluene azeotrope. The weight proportion of extractable material was measured for each sample in the laboratories of Polymer Corporation and is recorded in Table I). For each fraction are recorded the calculated weight, w, of each fraction, the weight fraction, w_x ($= w/W'$), and the viscosity functions $[\eta]$, β, and k'. In Table VI are the values of these viscosity functions for the unfractionated samples.

TABLE III

DATA FOR FRACTIONS OF RUBBER POLYMERIZED AT 50° C (RF-13)

W = 5.015 g. C = 1.003 g./100 cc. W' = 4.85 g.

Fraction	w(g.)	w_x ($\times 10^2$)	$[\eta]$	β	k'
1	0.2418	5.30	4.07_4	0.08_4	0.41_6
2	0.1784	3.89	3.39_6	0.12_9	0.37_1
3	0.2584	5.65	2.75_9	0.13_4	0.36_6
4	0.3090	6.74	2.31_2	0.15_2	0.34_8
5	0.3289	7.18	2.08_3	0.16_7	0.33_3
6	0.3320	7.29	1.76_6	0.16_8	0.33_2

TABLE IV

DATA FOR FRACTIONS OF RUBBER POLYMERIZED AT 40° C (RF-7)

W = 5.65 g. C = 1.13 g./100 cc. W' = 5.08 g.

Fraction	w(g.)	w_x ($\times 10^2$)	$[\eta]$	β	k'
1	0.2742	5.39	4.56_3	0.07_8	0.42_2
2	0.1911	3.76	3.38_6	0.09_8	0.40_2
3	0.2365	4.65	3.30_6	0.12_9	0.37_1
4	0.2090	4.12	2.59_6	0.17_1	0.32_9
5	0.2125	4.18	2.22_5	0.17_4	0.32_6
6	0.2843	5.60	2.10_8	0.16_6	0.33_4
7	0.3154	6.21	1.87_5	0.17_0	0.33_0

TABLE V

DATA FOR FRACTIONS OF RUBBER POLYMERIZED AT 30° C (RF-9)

W = 5.015 g. C = 1.003 g./100 cc. W' = 4.61 g.

Fraction	w(g.)	w_x ($\times 10^2$)	$[\eta]$	β	k'
1	0.2819	6.11	3.91_1	0.13_4	0.36_6
2	0.2147	4.66	3.34_8	0.16_1	0.33_9
3	0.2205	4.78	2.85_4	0.17_4	0.32_6
4	0.3289	7.13	2.51_1	0.16_9	0.33_1
5	0.3190	6.93	2.22_4	0.16_8	0.33_2
6	0.2364	5.15	1.87_7	0.17_1	0.33_0

In Figures 2, 4, 5, and 6, values of β and k' are plotted to emphasize deviations from the base value characteristic of unbranched species. At 50, 40, and 30° C, this value, which we shall represent with a bar under the symbol, seems to be the same as for the unbranched species of GR-S, namely, $\beta = 0.17_0 \pm 0.01$ and $k' = 0.33_0 \pm 0.01$. Unfortunately, the precision with which β can

Table VI

Data for Fractions of Rubber Polymerized at 15° C (RF-10)

$W = 5.015$ g. $C = 1.003$ g./100 cc. $W' = 4.54$ g.

Fraction	w(g.)	w_x ($\times 10^2$)	$[\eta]$	β	k'
1	0.1809	4.01	3.90_0	0.15_8	0.34_2
2	0.2024	4.50	2.84_5	0.14_8	0.35_2
3	0.2988	6.58	2.70_0	0.15_6	0.34_4
4	0.3360	7.40	2.27_0	0.15_7	0.34_3
5	0.3953	8.68	1.97_8	0.16_1	0.33_9
6	0.2878	6.34	1.77_2	0.16_0	0.34_0

be determined decreases as the intrinsic viscosity (and therefore the slope, $-\beta[\eta]^2$) decreases[18]. In the figures a rough indication of the precision of the measurement of β is given by the length of the vertical line through the point (at higher $[\eta]$ values such a line would be no longer than the diameter of the circle and is not drawn). Nevertheless, the selection of this base value seems justified by the data, especially since it agrees with that indicated by other experiments with similar rubbers prepared with different catalyst systems and at different rates[19]. At 15° C, the base value seems to be slightly different: $\beta = 0.15_6 \pm 0.01$), $k' = 0.34_4 \pm 0.01$. In each of these graphs the values of $[\eta]$ and β (and k') for the unfractionated sample are plotted for purposes of comparison.

Table VII

Intrinsic Viscosities and Slope Constants of Unfractionated Samples

ample	Temperature (° C)	$[\eta]$	β	k'
RF-8	50	1.58_8	0.15_0	0.35_0
RF-13	50	1.45_0	0.15_7	0.34_3
RF-7	40	1.86_0*	0.15_2	0.34_8
RF-9	30	1.60_6	0.14_8	0.35_4
RF-10	15	1.59_6	0.14_3	0.35_7

* This result is obviously in error, for all samples were prepared to very nearly the same intrinsic vistex but, unfortunately by the time a check determination was made, gel had appeared in the sample.

In Figure 2 the data are plotted for the two samples prepared at 50° C. These samples were not identical in origin and history; for RF-8, the time of reaction was slightly longer, the conversion slightly lower, and the initial thiol concentration lower. Nevertheless, one line seems to fit one set of points as well as it does the other. The fit is rather loose in both instances, it must be admitted. There is, however, more justification than is evident in this one figure for drawing a straight line through the points. In Figure 3, for example, are data for a sample prepared at the same temperature from a similar recipe, but at a faster rate (reaction time 3 hours). Here the points lie on or very close to a straight line. Moreover, in the later figures—4, 5, and 6—a family of straight lines seems to fit the data adequately.

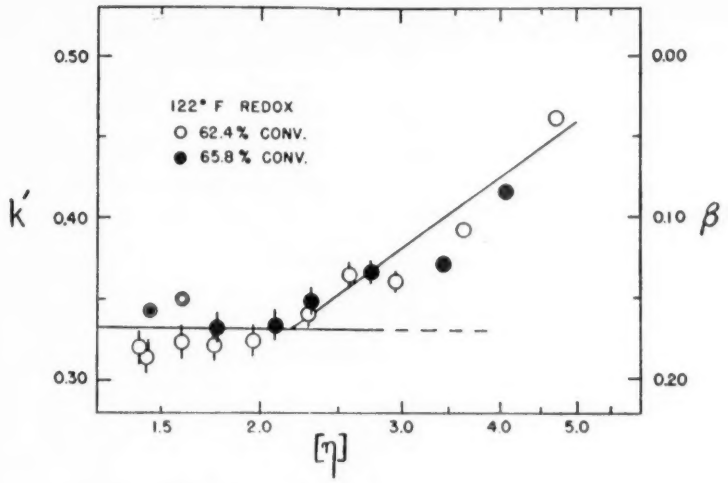


FIG. 2.—Variation of k' (and β) with $[\eta]$ for fractions of two rubber samples polymerized at 50° C. Double circle, unfractionated sample.

DISCUSSION

From Figure 2 it is evident that the slight differences of the two polymers prepared at the same temperature, 50° C, are not reflected in measurable differences in the k', $[\eta]$ behavior. The higher concentration of thiol has slightly reduced the intrinsic viscosity of the corresponding fractions, as of the whole polymer. But, at any given intrinsic viscosity, the slope constants have the same value, within experimental error. (This is in accord with the observations

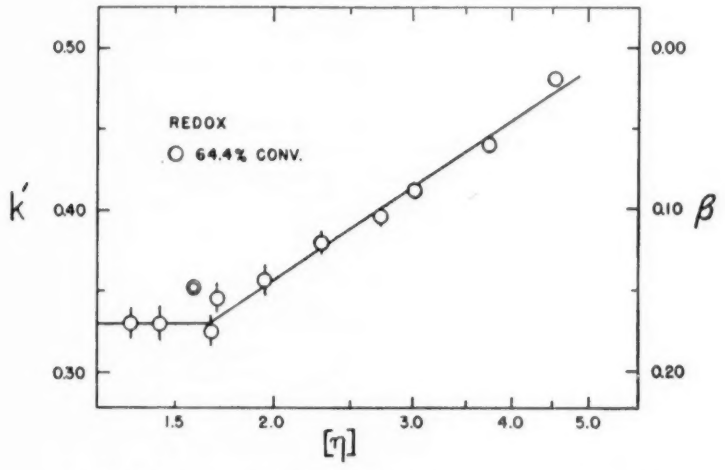


FIG. 3.—Variation of k' (and β) with $[\eta]$ for fractions of a rubber polymerized in 3 hours at 50° C. Double circle, unfractionated sample.

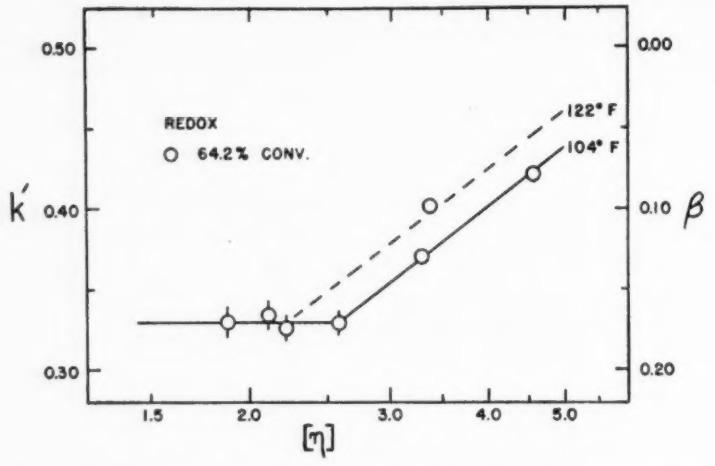


FIG. 4.—Variation of k' (and β) with $[\eta]$ for fractions of the rubber polymerized at 40° C.

that, with GR-S, the value of k' (and of β) at a given $[\eta]$ is practically independent of the conversion[4], and, since thiol content decreases with conversion, independent also of the thiol concentration.) Assuming that an increase in k' above the base value k' is an indication of branching and that the extent of the increase, $k' - k$, is a rough measure of the degree of branching, we conclude that, in species of lower molecular weight than that corresponding to $[\eta] = 2.0$, branching is too slight to be detectable, but that in species of higher molecular weight the degree of branching is greater, the higher the molecular weight.

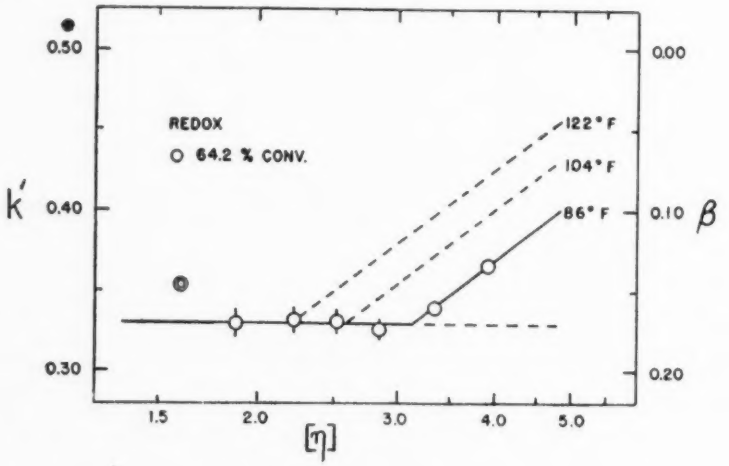


FIG. 5.—Variations of k' (and β) with $[\eta]$ for fractions of the rubber polymerized at 30° C. Double circle, unfractionated sample.

It is clear also that making measurements on fractions is much better than making them on the whole rubber. For one thing, the single value gives us no information about possible differences of degree of branching in species of different molecular weight; for another, the average effect measured in this way is so small that it could easily be attributed to experimental error (whereas the consistent trend observed in the values for higher fractions increases confidence in any one value).

Although a change in conversion does not seem to affect the degree of branching in species of a given molecular weight[14], it is evident from Figures 4, 5, and 6 that changing the temperature of polymerization does. The effect on branching is two-fold; with each successive decrease in polymerization temperature: (*a*) the molecular weight (strictly, intrinsic viscosity) of the species in which branching is just detectable increases and (*b*) the degree of branching, at

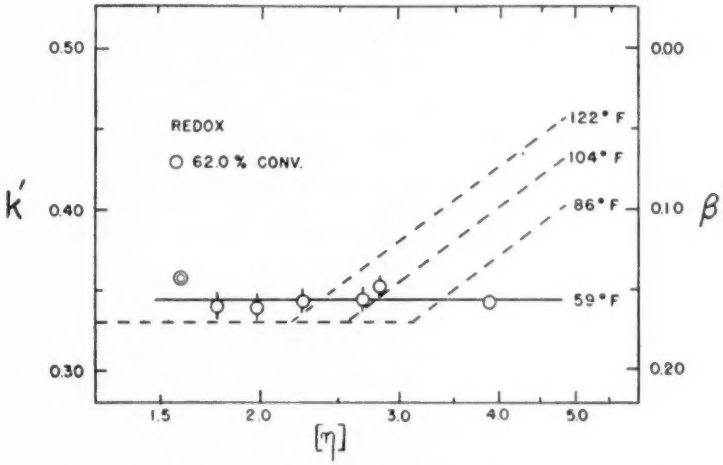


FIG. 6.—Variation of k' (and β) with $[\eta]$ for fractions of the rubber polymerized at 15° C. Double circle, unfractionated sample.

a given molecular weight, as measured by $k' - k'$, decreases. Eventually at 15° C (see Figure 6) branching has been so repressed that none of the fractions show any indication of it, *i.e.*, all have the same value of k'. (It might well be that branching would have been detected in fractions of intrinsic viscosity greater than 4.0 if a polymer of higher average molecular weight had been prepared.)

Branching, as we have been using the term, includes the nonlinearity produced both by the branching reaction[20] (free radical dehydrogenation of a growing or dead polymer molecule at a methylenic carbon adjacent to an internal double bond, and subsequent growth from this polymer radical) and by the cross-linking reaction[20] (addition of a growing free radical chain at a double bond either in a polymer chain or, more probably[21], in a side vinyl group, with subsequent growth of the resulting polymer radical). Until the cross-linking reaction has proceeded far enough to produce insoluble gel, the two types of nonlinearity would almost certainly be indistinguishable by such experiments as these[22]. Our data, therefore, do not permit drawing conclusions

regarding the effect of polymerization temperature on these two reactions separately. There is reason to believe, however, that most of the branching in diene polymers is due to the cross-linking reaction[23]. If this is so, we can conclude that decreasing the temperature of polymerization decreases the rate of the cross-linking reaction more than it does the rate of normal chain propagation. This qualitative conclusion is in agreement with the quantitative ones of Morton and Salatiello[24], who estimated that, for polybutadiene prepared in emulsion, the reactivity ratio [20] ($K = k_3/k_2$, where k_2 is the velocity constant for propagation, k_3 the velocity constant for cross-linking) decreased from about 2.0×10^{-4} at 60° C to about 1.0×10^{-4} at 40° C.

Decreasing the polymerization temperature decreases the rate of both reactions, of course. In order to make the rate of chain propagation about the same at all temperatures, the time of reaction, *i.e.*, the time required to reach the same intrinsic viscosity at the same conversion, was made the same at all temperatures. This was accomplished by making slight alterations in the recipe, using progressively weaker reducing agents at progressively higher temperatures. The effect of counterbalancing the two factors in this way should be the production of the same number of initiating free radicals in the same over-all time, and presumably at comparable rates. It seems reasonable to conclude that the differences in branching observed (or rather inferred from the evidence) are due in large part to the differences of polymerization temperature rather than to the slight changes of the composition of the reaction system.

Because a decrease of polymerization temperature is known to be responsible for other changes of molecular structure, notably an increase in the proportion of mers $\left[\begin{matrix} H & H & H & H \\ | & | & | & | \\ -C- & C= & C- & C- \\ | & & & | \\ H & & & H \end{matrix}\right]$ with the *trans*-configuration, objection might be made to our attributing the decreases of $k' - k'$ at a given $[\eta]$ entirely to decreases in branching. This interpretation seems justifiable for two reasons: (1) the effects observed here as a result of changes of polymerization temperature are very similar to those observed in polystyrene as a result of altering the proportion of copolymerized divinylbenzene[25], and (2) the change of k' is greatest where branching would be expected to be greatest, namely, in the high molecular-weight species, whereas a change in the proportion of *trans*-units in the chain should affect all species equally, regardless of molecular weight.

It is tempting, however, to attribute the decrease of the base value k' (or β) from 0.33_0 to 0.34_4 (at 15° C) to this increase of the proportion of *trans*-1,4 units. We already have evidence[19] that this trend to a higher base value continues at lower polymerization temperatures, becoming about 0.37 at 0° C. Since, unfortunately, this observation was made with a poly(butadiene-*co*-styrene) of higher (85:15) butadiene content, our experiments with 72:28 polymers are being extended to lower temperatures.

As Johnson and Wolfangel have also described a means of measuring branching in polymers and have used it to study the effect of polymerization temperature on branching[26], it is interesting to compare their method with ours. Both involve laborious and time-consuming fractionation but, whereas their method involves measurements of viscosity and osmotic pressure, ours requires only viscosity measurements. This is a distinct advantage, for obtaining reliable molecular weights osmometrically is notoriously difficult. Again, from the papers of Johnson and Wolfangel, it would appear to be impossible to obtain information about the degree of branching in a single fraction, as is possible by

our method, for each of the straight lines they obtain on a log $[\eta]$ *vs.* log M plot corresponds to a different sample, and is obtainable only by plotting the data for several fractions of that sample. Actually their interpretation of their data seems open to question. If, as they claim, and as seems reasonable, branching affects both k and a in the relation: $[\eta] = kM^a$, no one set of values of k and a should be applicable to all the fractions of a given sample containing branched species, for the degree of branching should be greater in the higher molecular weight species. Instead of a straight line on a log $[\eta]$ *vs.* log M plot, then, one should get a curve, following the line for linear polymer species at low molecular

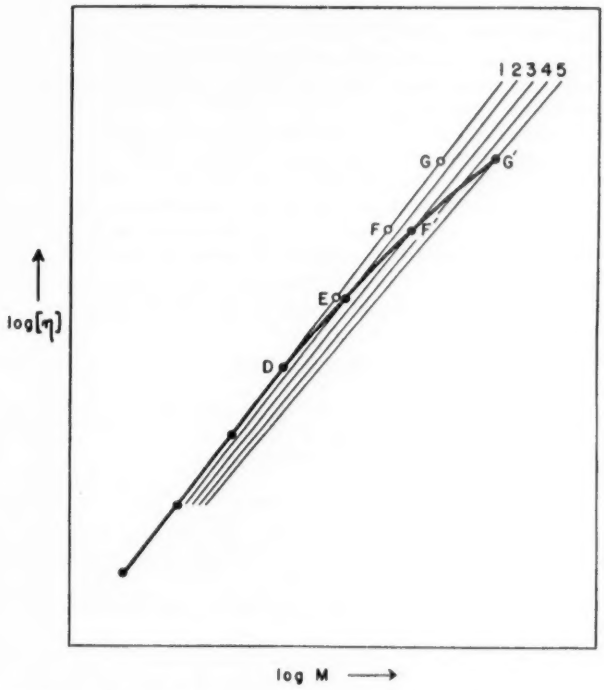


FIG. 7.—Hypothetical relations between $[\eta]$ and M for unbranched and branched species.

weights but diverging increasingly from it at higher molecular weights. [In Figure 7, line 1 represents the relation for linear species, and lines 2, 3, 4, and 5 those for species progressively more intensively branched. If all fractions consisted of linear species, the points would all fall on line 1 (as do A, B, C, D, E, F, G); if the fractions of higher intrinsic viscosity were progressively more branched the points would fall not on line 1 but on those farther and farther from it, *i.e.*, at E′, F′, and G′.] This is, indeed, what Thurmond and Zimm[27] observed in their experiments with cross-linked polystyrene. According to this reasoning, a rough measure of the degree of branching in a polymer could be obtained by measuring the distance of the point for that fraction from the line for linear species, *i.e.*, GG′, or FF′ in Figure 7. (For diene polymers the upper portion of this line might have to be obtained by extrapolation.)

In future work we plan to make a direct comparison of the two methods of measuring the degree of branching, by using both on the same polymer fractions.

SYNOPSIS

Samples of poly(butadiene-*co*-styrene)—all of charge ratio butadiene: styrene 72:28—were prepared in emulsion at 15, 30, 40, and 50° C. Essentially the same redox recipe was used for each, with slight modifications to produce in about the same time polymers of similar intrinsic vistex (1.9 to 2.0) at similar conversions (about 65 per cent) well below the gel point. Each sample was fractionated by precipitation from 1 per cent benzene solution with methanol, special pains being taken to obtain fractions of equal size (each around 5 per cent of the original rubber in the sample fractionated). Careful measurements of the viscosity functions $[\eta]$, β, and k' for each fraction were made; with every sample except that prepared at the lowest temperature, the values of β and k' were observed to deviate in the high molecular weight region from the "base value" common to lower fractions, the deviation starting at a lower molecular weight, and being greater at a given high molecular weight, the higher the temperature of polymerization. It is concluded that branching in a diene polymer of this type is repressed as the temperature of polymerization is decreased; the lower the temperature the higher is the molecular weight at which branching is detectable and the lower is the degree of branching at a given molecular weight. In the 15° C, rubber no branching was detectable at any molecular weight.

ACKNOWLEDGMENTS

We acknowledge with gratitude the assistance given us in this work by H. L. Williams and his associates, particularly M. Davidson, both by preparing the polymers for us and through helpful discussions.

REFERENCES

[1] Cragg and Manson, *J. Polymer Sci.* **9**, 265 (1952); Manson and Cragg, *Can. J. Chem.* **30**, 482 (1952).
[2] Cragg and Switzer, paper presented at Canadian High Polymer Forum, Hamilton, 1949; Cragg and Brown, *Can. J. Chem.* **30**, 1033 (1952); preceding article in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[3] Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1942); Mead and Fuoss, *J. Am. Chem. Soc.* **64**, 277 (1942).
[4] Meyer, *Ind. Eng. Chem.* **41**, 1570 (1949); Gehman, *Ind. Eng. Chem.* **44**, 730 (1952).
[5] Meyer, *Ind. Eng. Chem.* **41**, 1570 (1949).
[6] Hart and Meyer, *J. Am. Chem. Soc.* **71**, 1980 (1949).
[7] Johnson and Wolfangel, *Ind. Eng. Chem.* **41**, 1580 (1949).
[8] Gehman, *Ind. Eng. Chem.* **44**, 730 (1952).
[9] Bryant, *J. Polymer Sci.* **2**, 547 (1947); Richards, Cross, and Ray, *Discussions Faraday Soc.* **9**, 235 (1950).
[10] Meyer, *Ind. Eng. Chem.* **41**, 1570 (1949); Winkler and Brown, "Kinetic Studies of a Redox Polymerization", paper presented at the Canadian High Polymer Forum, Montreal, **1952**.
[11] Johnson and Wolfangel, *Ind. Eng. Chem.* **44**, 752 (1952).
[12] Johnson and Wolfangel, *Ind. Eng. Chem.* **44**, 752 (1952); Thurmond and Zimm, *J. Polymer Sci*, **8**, 477 (1952).
[13] Cragg and Switzer, paper presented at Canadian High Polymer Forum, Hamilton, **1949**.
[14] Cragg and Brown, *Can. J. Chem.* **30**, 133 (1952); preceding article in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.
[15] Henderson, D. A., and Legge, N. R. (Polymer Corporation, Sarnia), private communication.
[16] Cragg, Rogers and Henderson, *Can. J. Research* **B25**, 333 (1947).
[17] Ewart, E. H., in "Advances in Colloid Science", edited by Mark and Whitby, Interscience Publishers, Inc., New York, **1946**, Vol. 2.
[18] Manson and Cragg, *Can. J. Chem.* **30**, 482 (1952).
[19] Cragg, L. H., and Fern, G. R. H., unpublished data, McMaster University.
[20] Flory, *J. Am. Chem. Soc.* **69**, 2893 (1947).
[21] Sivertz, C. S., "The Life History of a Butadiene-Styrene Polymer Molecule", paper presented at the Canadian High Polymer Forum, Kingston, Ontario, May 1951.
[22] Walker and Winkler, *Can. J. Research* **B28**, 298 (1950).
[23] Sivertz, C. S., unpublished results, Univ. of Western Ontario, London, Ontario, **1951**.
[24] Morton and Salatiello, *J. Polymer Sci.* **6**, 225 (1951).
[25] Cragg and Manson, *J. Polymer Sci.* **9**, 265 (1952).
[26] Johnson and Wolfangel, *Ind. Eng. Chem.* **41**, 1580 (1949); *Ind. Eng. Chem.* **44**, 752 (1952).
[27] Thurmond and Zimm, *J. Polymer Sci.* **8**, 477 (1952).

STRUCTURAL CHANGES IN RUBBER CAUSED BY THE ACTION OF MOLECULAR OXYGEN. V. DESTRUCTIVE SOLUTION OF VULCANIZED SYNTHETIC RUBBERS *

Z. Tarasova and B. Dogadkin

In earlier papers[1] we described the destructive solution of vulcanized natural rubber and the properties of some of the byproducts which form as a result of this process. In these papers we showed that, under conditions of strict exclusion of oxygen, a vulcanizate does not dissolve in liquid hydrocarbons, even when heated at 140° C, and even when peptizing agents and polar compounds are added to the solvent. Heating causes dissolution of vulcanized rubber in a solvent only in the presence of molecular oxygen, and the process follows the scheme: absorption of oxygen → decomposition of molecular chains at the points of oxygen absorption → solution. When the surface area of the vulcanizate is maintained constant, the process goes on at a constant rate which depends on the temperature and partial pressure of the oxygen in the solvent. In general, the relation of the rate of destructive solution to the partial pressure of oxygen $\frac{dK_a}{d\tau}$ is expressed by the equation:

$$\frac{dK_a}{d\tau} = K\frac{\gamma P}{\gamma P + 1}$$

where K and γ are constants.

The degraded vulcanizate is of relatively low molecular weight (3600 according to the Lamma method), shows a characteristic light scattering, and follows a concentration law which conforms to the Einstein viscometric equation through a wide range. This is proof that, during destructive solution, massive particles, comprising fragments from the spatial chains of the vulcanizate, pass into solution.

The present work describes experiments which show that destructive solution takes place also with vulcanized synthetic rubbers.

(1) *The influence of the nature of the rubber on the kinetics of the process of destructive solution of vulcanizates.*—Vulcanizates of sodium-butadiene, butadiene-styrene, chloroprene, and Butyl rubbers were dissolved.

The vulcanized films were prepared from benzene solutions on the surface of glass ampules according to the method described earlier[2]. The vulcanizates of sodium-butadiene and butadiene-styrene rubber had the following composition: rubber 100, sulfur 2, thiuram 0.3, zinc oxide 1, stearic acid 1. The optimum vulcanization at 143° C was 30 minutes. The polychloroprene (Neoprene) vulcanizate was prepared from a mixture of the following composition: rubber 100, mangesium oxide 3, rosin 3, zinc oxide 3. In this case the mixture was dissolved in dichloroethane. The optimum vulcanization at 143° C was

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Zhurnal Obshchei Khimii* (*Journal of General Chemistry*), Vol. 22, pages 935–945 (1952).

30 minutes. The Butyl vulcanizate had the following composition: rubber 100, sulfur 2, thiuram 1, zinc oxide 2, stearic acid 2.

The vulcanized films showed mechanical properties typical of normal vulcanizates of the same compositions. It should be noted that the composition of a rubber film prepared from the same cement changed somewhat with time as a result of settling of undissolved ingredients. Consequently in each series of experiments the films were prepared at the same time.

Heating a film of vulcanized sodium-butadiene rubber in xylene, with oxygen carefully removed, up to 140° C resulted in no appreciable solution. At the same time, the vulcanized synthetic rubbers mentioned above dissolved completely when heated in the same solvent saturated with molecular oxygen.

The experiments on destructive solution were carried out according to the method used previously[2]. The kinetics of destructive solution of vulcanized rubbers (Figure 1) is represented by a uniform curve with a linear beginning

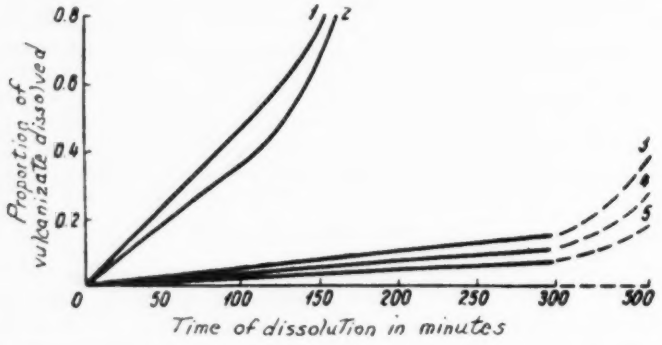


FIG. 1.—Kinetic curves of destructive solution of vulcanized rubbers. Temperature 110° C, oxygen pressure 760 mm. Hg. 1. Natural rubber. 2. Polychloroprene rubber (Neoprene). 3. Butadiene-styrene rubber. 4. Sodium-butadiene rubber. 5. Butyl rubber.

which indicates the period when the reacting surface remains constant. Immediately after this period, a sharp increase of the rate of reaction appears as a result of the increase of surface area because of the mechanical destruction of the sheet and passage of parts of it into solution, which exposes new surface areas.

In accordance with the above, the whole process of destructive solution of finely divided rubber is expressed by a straight line. We did not, however, use this method, since even when the rubber is carefully cut, the surface area is variable.

As was expected, the rate of destructive solution depends on the molecular structure of the rubber (see Table 1). Based on their rates of destructive solution, different types of vulcanized rubber can be classified thus in increasing order: Butyl rubber < sodium-butadiene rubber < butadiene-styrene rubber < polychloroprene < natural rubber. For rubbers which contain no polar groups in their molecules, this order corresponds to the concentration of double bonds in the main chains of the polymers. The presence of polar groups retards the process of oxidative destruction, *e.g.*, vulcanized polychloroprene dissolves more slowly than does vulcanized natural rubber, although the double

bond contents of the molecular chains of the two types of rubber are the same. The retarded solution of vulcanized butadiene rubbers is explained by their characteristic structures.

At temperatures at which there is no thermal destruction, passage into solution of vulcanized rubbers when heated in a solvent saturated with oxygen is caused by structural degradation of the vulcanizate at the double bonds, with consequent passage into solution of the fragments, which accompanies the reaction of oxygen with the molecular chains of the spatial structure.

The molecules of natural rubber and polychloroprene are of such a structure that the monomeric groups are united in the 1,4-position with respect to the linear chain. It may be assumed that every process of oxidation leads to the rupture of the double bonds and, in turn, to rupture of the chains and decrease of the molecular weight. In the molecules of sodium-butadiene and butadiene-styrene rubbers, the monomeric groups are united at the 1,4- and the 1,2-positions. The double bonds are located in the main chain as well as in the side vinyl groups, and in sodium-butadiene rubber there are about 40 per cent of 1,4-type bonds and 60 per cent of 1,2-type bonds.

TABLE 1

RELATION OF RATE OF DESTRUCTIVE SOLUTION OF VULCANIZATES TO THE COMPOSITION AND STRUCTURE OF RUBBER

No.	Rubber	Temperature (° C)	Content of 1,4-structure (%)	Rate of destructive solution (g. per sq. cm. per min.)
1.	Smoked sheet	110°	100	4.95×10^{-5}
2.	Polychloroprene (Neoprene)	110°	100	3.8×10^{-5}
3.	Butadiene-styrene rubber	110°	—	4.0×10^{-6}
4.	Sodium-butadiene rubber	110°	43	3.2×10^{-6}
5.	Butyl rubber	110°	100	3.0×10^{-6}
6.	Smoked sheet	120°	100	6.75×10^{-5}
7.	Butadiene rubber	120°	59	2.7×10^{-5}
8.	Butadiene rubber	120°	54	1.1×10^{-5}
9.	Butadiene rubber	120°	43	0.62×10^{-5}

It is quite clear that oxidation and rupture of the double bonds of the side vinyl groups do not cause degradation of the spatial structure of a vulcanizate. Furthermore, as Dogadkin has shown[3], the action of oxygen on the side vinyl groups causes a process of structure formation, inasmuch as polyfunctional molecular chains are formed from the oxidation of the side vinyl groups, without decrease of the initial molecular weight, whose oxygen groups are able to react with one another and with the double bonds of the polymer, forming chemical and local intermolecular (hydrogen, orientation) bonds. If to this is added the possibility of polymerization processes caused by the action of peroxide compounds, and at high temperatures, the effect of heating itself, then it becomes understandable that the effectiveness of the destructive action of oxygen in the case of vulcanizates of butadiene polymers containing side vinyl groups decreases considerably. The importance of any difference of position of the double bonds in molecular chains of rubber during destructive solution appears clearly in the case of butadiene polymers containing differing amounts of 1,4- and 1,2-structures.

Rubbers which, according to data on the kinetics of their reaction with perbenzoic acid (Prilezhayev reaction), contained 59, 54, and 43 per cent of 1,4-structure, were used. The vulcanizates were prepared from the same recipe

as for the natural-rubber vulcanizate, in which the 1,4-structure content was 100 per cent. From Figure 2 we see that the rate of destructive solution of these vulcanizates is a linear function of the double bond content in the main chains (1,4-structure). The fact that the curve of the rate of solution as a function of the number of double bonds of the 1,4-structure type does not pass through the origin of the coordinates shows that the double bonds in the side vinyl groups of 1,2-type structure cause a temporary process of structure formation. As long as the oxygen concentration in the system remains constant, the kinetics of the process can be formulated thus. The rate of degradation of the molecular chains v_1 is proportional to the concentration C of double bonds of the 1,4-structure:

$$v_1 = k_1 C \tag{1}$$

and the rate v_2 of the processes of structure formation is proportional to the concentration $C_2 = (1 - C)$ of double bonds of the 1,2-structure:

$$v_2 = k_2(1 - C) \tag{2}$$

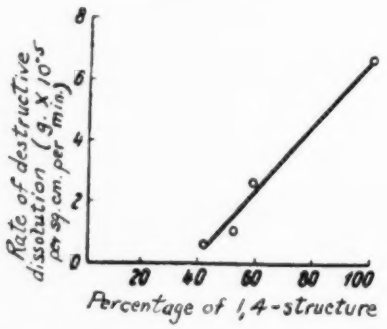


FIG. 2.—Relation of rate of destructive solution of vulcanized butadiene rubber to content of 1,4-structure. Temperature 120° C, oxygen pressure 760 mm. Hg.

Then the integral rate V of destructive solution is the algebraic sum of the rates of both processes:

$$V = v_1 - v_2 = -k_2 = (k_1 + k_2)C \tag{3}$$

As we showed earlier[2], the solution process takes place on the surface layer at a constant rate, which depends on the initial concentration of double bonds. Consequently Equation (3) is valid for the whole process if the surface area of the destroyed vulcanizate remains constant. The constants of Equation (3) depend on the temperature, partial pressure, and coefficient of absorption of oxygen in the solvent. For the case of solution in xylene of unloaded vulcanizates, containing as accelerator tetramethylthiuram disulfide, at an oxygen pressure of 760 mm. and temperature of 120° C, Equation (3) can be represented as:

$$V = -4.0 \times 10^{-6} + 1.2 \times 10^{-7} C \tag{4}$$

where V is expressed in grams per sq. cm. per min. and C in percentage of double bonds of the 1,4-structure type in the total quantity of double bonds in the polymer. This relation enables us to determine experimentally the con-

tents of 1,2- and 1,4-structures in the molecules of butadiene polymers according to the rate of destructive solution.

The influence of the structure of a polymer is also evident by the amount of energy of activation in the process of destructive solution. In order to measure this energy, it is necessary to determine the temperature change of the coefficient of absorption of oxygen in the solvent. The authors, together with Reznikovskiĭ[4], established that the absorption coefficient of oxygen in xylene in the temperature range of 23°–100° C increases according to the following linear equation:

$$l^{T}_{A} = 150.5 + 0.395t \tag{5}$$

The kinetics of solution of the vulcanizate conforms to the equation:

$$\frac{dK_a}{dt} = k[O]S \tag{6}$$

where $[O]$ is the concentration of oxygen in the solvent and S is the surface area of the vulcanizate.

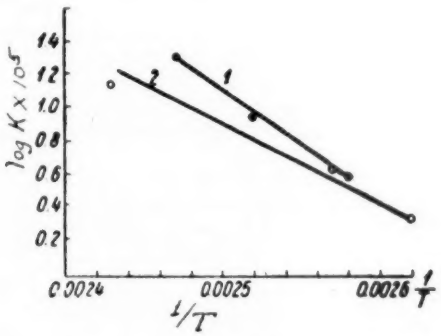


FIG. 3.—Temperature relation of the kinetic constants of the process of destructive solution of vulcanizates. 1. Sodium-butadiene rubber. 2. Butadiene-styrene rubber.

If the values of $[O]$ calculated from Equation (5) are substituted in this equation, the kinetic constants obtained for various temperatures follow in an approximate way Arrhenius' equation (Figure 3). The apparent energy of activation of destructive solution of vulcanized natural rubber in the temperature range of 87°–107° C is 19 kcal. per mole, of vulcanized sodium-butadiene rubber in the temperature range of 116°–228° C it is 31.2 kcal. per mole, and of butadiene-styrene rubber in the temperature range of 114°–123° C, it is 27.12 kcal. per mole.

The much greater energy of activation of natural rubber compared with that of butadiene polymers is explained by the presence of double bonds in their side vinyl groups, which direct the process toward spatial structural formation.

2. *Influence of the composition of a vulcanizate on the kinetics of its destructive solution.*—The influence of the vulcanizing agent on the kinetics of solution of vulcanized natural rubber was studied. The composition and quantity of the other ingredients of the original recipe (see above) were not changed.

Although not changing the character of the kinetics of the process (see Figure 4), a change of composition of the vulcanizing agent causes a change of

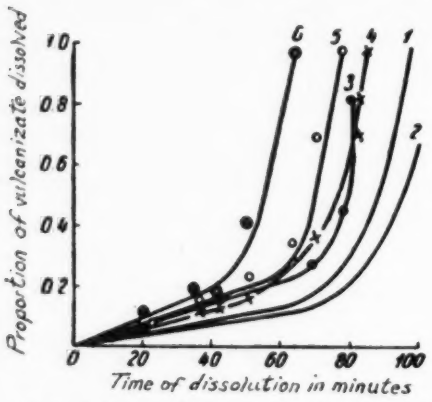


FIG. 4.—Kinetic curves of the destructive solution of vulcanized natural rubber containing different vulcanization accelerators. Temperature 109° C. 1. Captax. 2. Santocure. 3. Zimate. 4. Vulcacit P/R. 5. Tetramethylthiuram disulfide. 6. Diphenylguanadine.

the rate of destructive solution (Table 2), independent of the mechanical properties of the vulcanized film and the content of bound sulfur. Since the degree of vulcanization of the experimental mixtures was identical, the influence of the composition of the vulcanizing agent on the rate of destructive solution can be ascribed to the chemical nature of the accelerator.

TABLE 2

DEPENDENCE OF RATE OF DESTRUCTIVE SOLUTION OF VULCANIZED NATURAL RUBBER ON THE COMPOSITION OF THE VULCANIZING AGENT

Temperature, 109° C, Oxygen pressure, 760 mm. Hg

Composition of vulcanizing agent by weight	Tensile strength (kg. per sq. cm.)	Relative elongation (%)	Residual elongation (%)	Rate of solution ($r \times 10^5$ sq. cm. per min.)	Bound sulfur (%)
Thiuram 0.2 Sulfur 2.0	176	840	6	3.0	1.48
Captax 0.8 Sulfur 2.75	221	850	12	3.87	1.47
Diphenylguanidine 10 Sulfur 8.5	190	880	8	2.31	1.35
Zimate 0.3 Sulfur —	180	830	8	3.6	—
Vulcacit 0.25 Sulfur 2.0	180	950	8	3.4	—
Santocure 1.0 Sulfur 2.0	314	765	12	4.9	1.48

We showed earlier[2] that thiols accelerate the solution of vulcanized natural rubber, while amines retard this process. It is also known[5] that tetramethylthiuram disulfide retards oxidation. In fact, rubbers dissolve relatively slowly when they contain a thiuram compound and diphenylguanidine. Accelerators which contain a mercapto group accelerate the solution of rubbers. This can be attributed to the fact that thiols in certain cases accelerate the adsorption of oxygen and also inhibit the polymerization processes.

It must be borne in mind that, by this method, films of vulcanizates extracted in chloroform also dissolved; this removes all of the accelerators which

did not react during vulcanization. Consequently in the experiments described, the accelerator or its byproducts present in the combined state in the vulcanizate also appear to influence the rate of destructive solution.

3. *Influence of the nature of the solvent on the kinetics of destructive solution of vulcanized sodium-butadiene rubber.*—Figure 5 shows the kinetic curves of destructive solution of vulcanized sodium-butadiene rubber in various solvents: xylene, "white spirit," benzine, ligroine, and toluene. The nature of the kinetic process is the same, but the rates of solution are different. In view of the

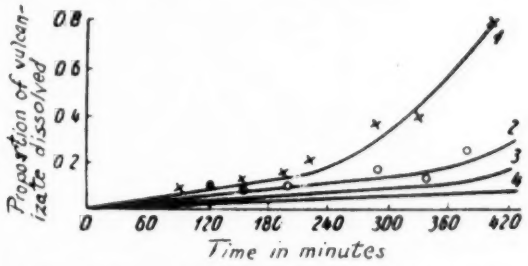


FIG. 5.—Kinetic curves of destructive solution of vulcanized sodium-butadiene rubber in various solvents. Temperature 110° C. 1. Xylene. 2. Ligroine. 3. Toluene. 4. "White spirit."

fact that the process of destructive solution depends on the action of oxygen, it may be assumed that these differences depend on differing solubilities of oxygen in the particular solvents.

As has been referred to before, in order to measure the solubility of oxygen in organic solvents, a special apparatus was constructed[4]. In distinction from the experiments described earlier, the preliminary degassing was effected in the apparatus itself, and the degassed solvent was passed into the adsorption vessel by its own vapor pressure.

TABLE 3

DEPENDENCE OF RATE OF DESTRUCTIVE SOLUTION OF VULCANIZED SODIUM-BUTADIENE RUBBER ON THE SOLUBILITY OF OXYGEN IN THE SOLVENT

Solvent	Temperature of destructive solution of vulcanizate	Rate of solution of vulcanizate (g. per sq. cm.)	Temperature of measurement of solubility of oxygen	Solubility of oxygen (in cc.) per 1 cc. of solvent
Xylene	110° C	6.3×10^{-6}	23.5	0.177
Ligroine	110°	4.6×10^{-6}	20	0.156
Toluene	110°	3.05×10^{-6}	20	0.129
"White spirit"	114°	1.72×10^{-6}	19	0.170

Figure 6 shows that the rate of destructive solution of vulcanizates is a linear function of the solubility of oxygen in the solvents. "White spirit" is the only exception. The delayed solution of the vulcanizate in this solvent seems to be due to the 10 per cent of aromatic compounds present in it; these may contain functional groups which retard the oxidation reaction.

4. *Influence of water on the kinetics of destructive solution of vulcanized sodium-butadiene rubber.*—Experiments on the influence of water were performed by the same method with the difference, that instead of dry oxygen, oxygen saturated with water vapor was introduced into the apparatus. The presence of

water in the oxygen and in the solvent does not change the nature of the kinetics of destructive solution of vulcanized natural and sodium-butadiene rubbers (Figure 7); in both cases it retards solution.

To explain the mechanism of the action of water during destructive solution, we performed experiments to determine the influence of moisture on the kinet-

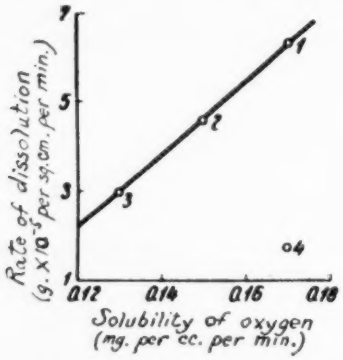


FIG. 6.—Influence of the solubility of oxygen in various solvents on the rate of destruction of vulcanized-sodium butadiene rubber. 1. Xylene. 2. Ligroine. 3. Toluene. 4. "White spirit."

ics of oxidation of vulcanized rubbers in the form of films. Oxidation was effected in a Nekrasov adsorption apparatus; the reaction vessels naturally did not contain any alkaline absorbents of the volatile products of oxidation. Water was added to the vessel thus: 1–2 drops of water was frozen in the vessel,

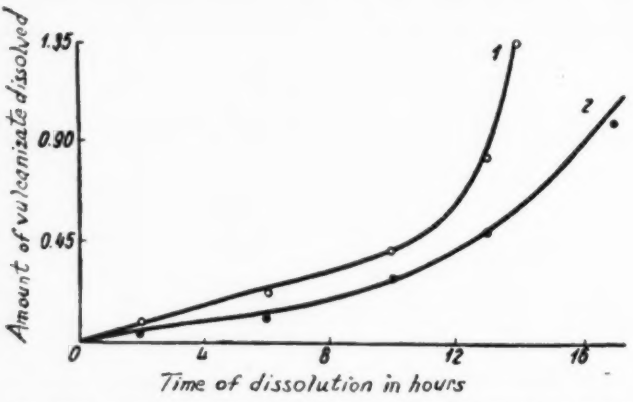


FIG. 7.—Effect of moisture on the kinetics of destructive solution of vulcanized sodium-butadiene rubber. Temperature 105° C. 1. Dry oxygen. 2. Oxygen containing water vapor at partial pressure 22.4 mm. Hg.

and then air was pumped out of the vessel and dry oxygen was added in inverse proportion to the increase of volume of the gas and water during the temperature rise. The oxidation in dry oxygen (also without alkaline absorbents) was carried out analogously. The films of vulcanized rubber were prepared by applying rubber cement and were vulcanized by the usual procedure.

These experiments showed (see Figure 8) that the presence of water in the oxygen in percentage corresponding to the partial pressure for the particular temperature retards absorption of oxygen, at least in the oxidation period of the vulcanizate following the induction period, evidently as a result of the destruc-

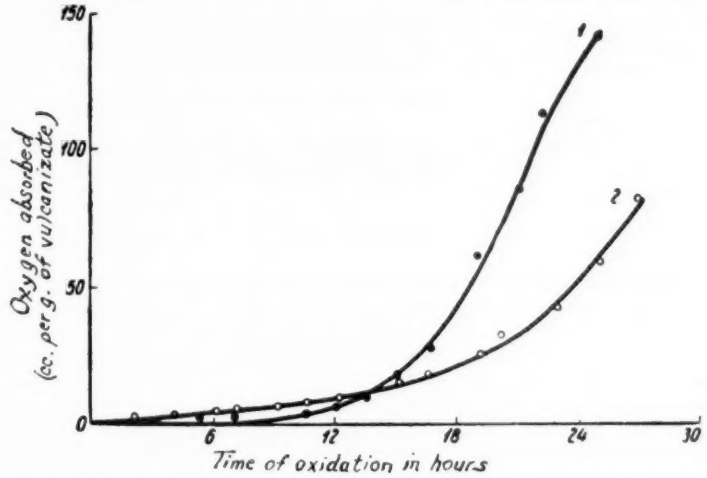


FIG. 8.—Influence of humidity on the kinetics of absorption of oxygen by vulcanized natural rubber. Temperature 108° C. 1. Dry oxygen. 2. Moist oxygen.

tion of peroxides by the water. Thus the retarding action of water on the dissolution of a vulcanizate is the result of a retarding action by water of the process of absorption of oxygen in rubber.

5. *Properties of destroyed vulcanized sodium-butadiene rubber.*—By the destructive solution of vulcanized sodium-butadiene rubber, a pale yellow opales-

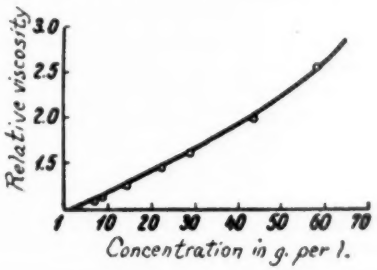


FIG. 9.—Relation of viscosity of solutions of destroyed vulcanizate of sodium-butadiene rubber to concentration.

cent solution is formed. Methyl alcohol (not less than 5 per cent solution) precipitates about 70 per cent of the substance as a viscous mass, which, after drying in a vacuum at room temperature, dissolves completely in all ordinary rubber solvents. Chemical analysis of the destroyed vulcanizate shows the presence of free carboxyl groups (5.4 mg. of carboxyl oxygen per gram of vulcanizate), ether groups (12 mg. of oxygen to 1 gram of vulcanizate), and per-

oxidic groups (1.2 per cent of the active oxygen). The total oxygen content in the destroyed vulcanizate (after separation by methyl alcohol) is about 4 per cent.

The weight of a particle of destroyed vulcanizate is measured by the cryoscopic method in benzene solutions of not less than 2 per cent concentration. This weight lies between 3600 and 2400, and tends to increase with decrease of the concentration of the solution. The osmotic particle weight, extrapolated to zero concentration, is 16,000. Unquestionably this represents the high-molecular fraction of the product, in view of the permeability of the membrane for the low-molecular fraction.

The viscosity of solutions of a destroyed vulcanizate of sodium-butadiene rubber (Figure 9) within these wide concentration limits follows the linear equation:

$$\eta_{sp} = 24.0\ V\ C \tag{7}$$

where η_{sp} is the specific viscosity, V is the specific volume of the vulcanizate, and C is the concentration in grams per liter. From the numerical coefficient of this equation, with the Simha table one can calculate the axial ratios of the ellipsoid[6] of rotation corresponding to the volumes of the particles of destroyed vulcanizate. It is 15. For molecules of raw sodium-butadiene rubber this relation, according to Pasynskiĭ's data[7], is 65.

The coefficient of Equation (7) is approximately 10 times as great as that of the Einstein equation; this proves that the actual volume of the particles of destroyed vulcanizate in solution is 10 times greater than their volume in the solid state. We know that the volume of the original vulcanizate in xylene increases in the proportion 9.8:1. A comparison of these values indicates that in the solution of destroyed vulcanizate there are huge particles which swell in the solvent, fragments, as it were, of the spatial structure of the vulcanizate.

Thus a solution of this type of a destroyed vulcanizate is a new type of lyophillic colloid system. The system described has certain features (shape, presence of an interface) of lyophobic colloids, and these characteristics distinguish it from solutions of ordinary high-molecular compounds. The conditions for stabilization, which are determined by the swelling property of the particles in the solvent, distinguish it from typical lyophillic colloids. Furthermore, the primary particles of the disperse phase of a solution of destroyed vulcanizate form an atomic system, united by the forces of primary valences. It is thus distinct from a system of particles of the disperse phase of lyophobic colloids.

CONCLUSIONS

1. Vulcanized synthetic rubbers, when heated in a hydrocarbon medium containing molecular oxygen, dissolve completely. The kinetics of destructive solution of vulcanized synthetic rubbers follows the pattern established for the destructive solution of vulcanized natural rubber.

2. The rate of destructive solution of a vulcanizate depends on the molecular structure of the rubber. Rubbers are classified in the following order according to the increase of rate of solution of their vulcanizates: Butyl rubber < sodium-butadiene rubber < butadiene-styrene rubber < polychloroprene < natural rubber. The apparent energy of activation of natural rubber is 19 kcal. per mole, for sodium-butadiene rubber 31.2 kcal. per mole, and for butadiene-styrene rubber 27.1 kcal. per mole.

3. The rate of destructive solution of vulcanized butadiene rubbers depends linearly on the extent of 1,4-structure in the rubber molecule.

4. The mechanical properties of vulcanizates do not appreciably influence the rate of their destructive solution. The type of accelerator used, however, is of essential importance; in fact, its influence corresponds to its influence on the rate of absorption of oxygen.

5. The presence of water slows down the dissolution of vulcanizates of natural and sodium-butadiene rubbers, since it retards their absorption of oxygen.

6. The rate of destructive solution of a vulcanizate in various solvents depends linearly on the coefficient of absorption of oxygen in the solvents.

7. The viscosity of a solution of decomposed vulcanized sodium-butadiene rubber depends linearly on the concentration up to 50 per cent.

8. The mean specific molecular weight, measured cryoscopically, of sodium-butadiene rubber was 2400– 3600, and the osmotic weight, 16,000. The axial ratio of the particles was 1:15.

9. The hypothesis is advanced that solutions of decomposed vulcanizates constitute a special type of colloid solution.

REFERENCES

[1] Dogadkin and Tarasova, *Zhur. Obshchei Khim.* **17**, 1402 (1947); Dogadkin, Tarasova, and Pasynskii, *Zhur. Obshchei Khim.* **17**, 2222 (1947).
[2] Dogadkin and Tarasova, *Zhur. Obshchei Khim.* **17**, 1402 (1947).
[3] Dogadkin, *Zhur. Obshchei Khim.* **15**, 177 (1945).
[4] Reznikovskii, Tarasova, and Dogadkin, *Zhur. Obshchei Khim.* **20**, 63 (1950).
[5] Dogadkin, Karmin, Dobromyslova, and Sapozhkova, *Kolloid. Zhur.* **10**, 268 (1948).
[6] Mehl, Oncley, and Simha, *Science* **92**, 132 (1940).
[7] Gotovskaya and Pasynskii, *Zhur. Fiz. Khim.* **20**, 715 (1946).

DEGRADATION OF NATURAL RUBBER IN SOLUTION IN VACUO *

W. F. WATSON

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTS, ENGLAND

Changes in the molecular state of natural rubber are now recognized to be induced by a variety of factors, *e.g.*, oxygen, ozone, water vapor, and irradiation by visible and ultraviolet light. With highly purified rubber hydrocarbon, the molecular degradation arising in the presence of oxygen is intimately associated with autoxidation[1]. This mechanism of degradation, related to hydroperoxide formation, has frequently been extrapolated beyond its tested validity to account for the degradation of raw and even vulcanized rubber. Of particular interest in connection with the present work, the decrease of viscosity of solutions of unpurified rubber has been widely ascribed to oxidation. However, rubber solutions kept *in vacuo* decrease in viscosity almost as rapidly as in oxygen. An experimental account of this degradation of natural rubber in solution *in vacuo* is described below, and an interpretation of the phenomenon is advanced.

EXPERIMENTAL METHODS AND MATERIALS

Rubber.—Smoked sheet was obtained specially from the Rubber Research Institute, Malaya, in order that its history be known. Latex was coagulated by formic acid, then washed and dried for 4 days in a smoke-house. It was stored in the dark at room humidity, the Mooney viscosity remaining at 66 and no gel developing during 6 months. For experiments with purified rubber, crepe and deproteinized coagula were fractionally precipitated from petroleum ether-benzene by acetone. Acetone was slowly added to 2 per cent rubber in 1:4 benzene:80°–100° C petroleum ether till a small first fraction precipitated overnight at 0° C. A middle fraction containing approximately 60 per cent of the rubber was then precipitated by acetone, and methanol if necessary. This middle fraction was redissolved and similarly reprecipitated. The precipitate, dried under 10^{-3} mm. Hg pressure to constant weight after 100 hours, gave oxygen and nitrogen contents lower than 0.25 and 0.02 per cent, respectively.

Solvents.—Laboratory-grade chlorobenzene was dried over calcium chloride and redistilled; the middle fraction of the distillate was used. Other solvents were similarly dried and redistilled. Acetic and mono- and trichloracetic acids were purified by partially crystallizing and decanting four times.

Methods.—The degradation of rubber in solution was usually measured by vacuum viscometers. These had B.S. specifications for the upper volume and capillary dimensions. The lower bulb was fashioned from a 250-cc. flask, the neck of which connected by a T-branch to a 50-cc. bulb above the calibrated volume. Vacuum viscometers with B.S. Grade 1 specifications were used for concentrations up to 0.5 gram rubber per 100 cc. solvent. The standard pro-

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 4, pages 202–214, August 1953.

cedure was to add 50 cc. solution to the viscometer, and then alternately evacuate to at least 10^{-4} mm. Hg pressure while cooling in CO_2-acetone and warm to room temperature four times before sealing off. A glass spiral attached above the sealing-off point and cooled in liquid air ensured no loss of solvent. The filled viscometers were immersed in liquid paraffin thermostatted to $\pm 0.05°$ C for known periods at the reaction temperature, the viscosity being determined at 25° C. Any variation of this technique is obvious from the text. Solution viscosities are expressed in the conventional unit, reduced specific viscosity, $\eta_{sp}/c = t - t_s/t_s \cdot c$, where t and t_s are times of flow of solution and solvent, respectively, and c is the rubber concentration in grams per 100 cc. solvent.

EXPERIMENTAL RESULTS

Degradation in vacuo and in oxygen.—The viscosity of a solution of rubber kept *in vacuo* at 25°–120° C decreased to a final constant value (*cf.* Figure 1). In view of the exceedingly small amount of oxygen which would be sufficient to induce degradation if it did so efficiently, it was essential at the outset to eliminate the possibility that the degradation observed after evacuation was due to residual oxygen. The following observations indicate this: (1) Exposure of the solution to oxygen after attaining the final reduced viscosity and subsequent degassing produced no further decrease in viscosity. (2) Reduced degradation in solution occurred after cold and hot mastication and partial gelling of the

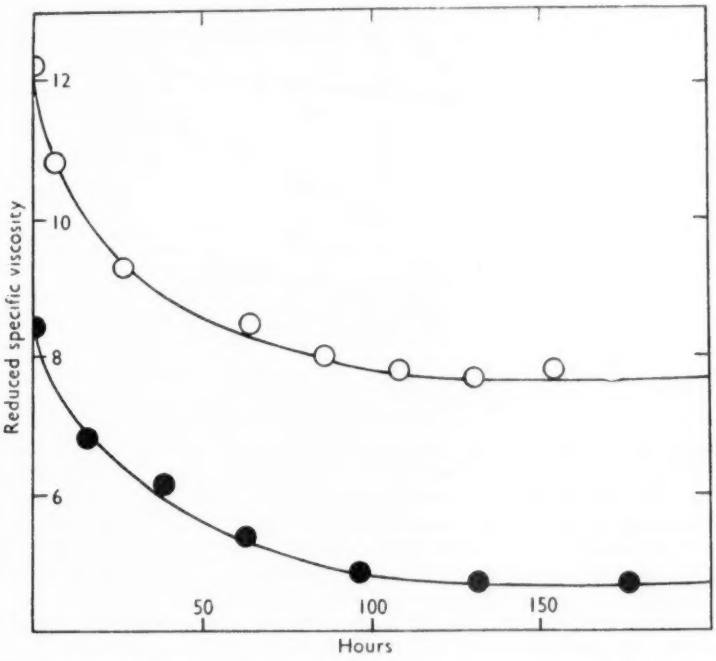


FIG. 1.—The decrease in viscosity of smoked sheet in chlorobenzene at 100° C *in vacuo*. —○— and —●— - - - 0.253 and 0.151 g. rubber/100 cc. chlorobenzene, respectively.

rubber. (3) No difference of rate of degradation was observed when solutions were sealed up under oxygen pressures of 10^{-4}–10^{-2} mm. Hg. (4) Addition of oxidation inhibitors, 0.05 per cent hydroquinone and 0.1 per cent pyrogallol[2], sufficient to reduce any oxidation to a small fraction of its value produced no decrease in rate of degradation at 100° C. (5) Rubber and gutta-percha degraded at rates independent of the extent to which (*a*) natural antioxidants were removed, and (*b*) the hydroperoxide content was increased by autoxidation.

The possibility that changes in viscosity could be attributed to other changes of the polymeric molecules, *e.g.*, cyclization, was eliminated by direct

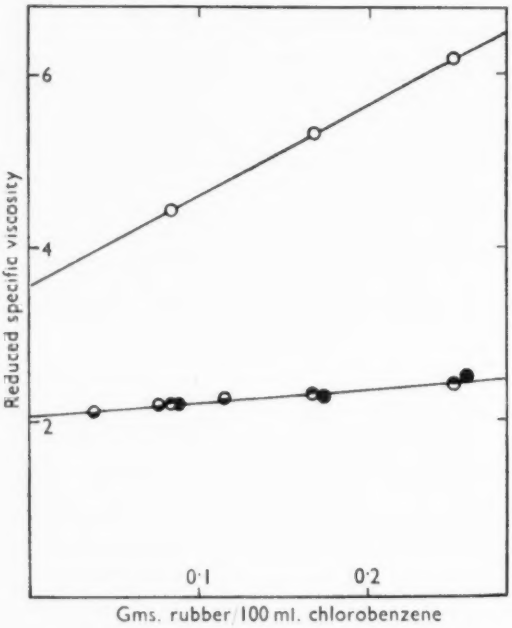


FIG. 2.—Viscosities of initial and degraded rubbers.

—○— - - - initial rubber.
—◎— - - - 0.115 g./100 cc. at 120° C.
—◉— - - - 0.248 g./100 cc. at 120° C.
—●— - - - 0.257 g./100 cc. at 100° C.

measurement of the decrease in number-average molecular weight; smoked sheet of initial molecular weight $\geq 2.5 \times 10^6$ decreased to 0.67×10^6 on being kept at 100° C until the viscosity remained constant. (The experimental technique was to seal up 2 grams of rubber in 200 cc. of chlorobenzene in B.S. Grade 3 viscometers, follow the degradation viscometrically to constant viscosity, change to benzene as solvent, and then determine the molecular weight with a Fuoss and Mead osmometer.)

Two possibilities could account for the final constant viscosity. It might denote the limit of degradation with the production of a thermally stable rubber, or an equilibrium of dissociation and combination reactions. The first of these is evidently correct, since (1) concentrating the solution by distilling off solvent

(chlorobenzene) produced no further change in viscosity with time when again evacuated and kept at the reaction temperature; (2) change of reaction temperature from 100°–120° C after attaining the final viscosity produced no viscosity change; and (3) addition of thiophenol and benzoquinone did not affect the final reduced viscosity, as they would if radical dissociation and combination were occurring[3].

The limit of degradation *in vacuo* of a rubber sample was found to be the same for different temperatures and for different concentrations of rubber. This is shown by the identity of the intrinsic viscosities and slopes of the reduced specific viscosity *vs.* concentration curves for degradation under different conditions (Figure 2).

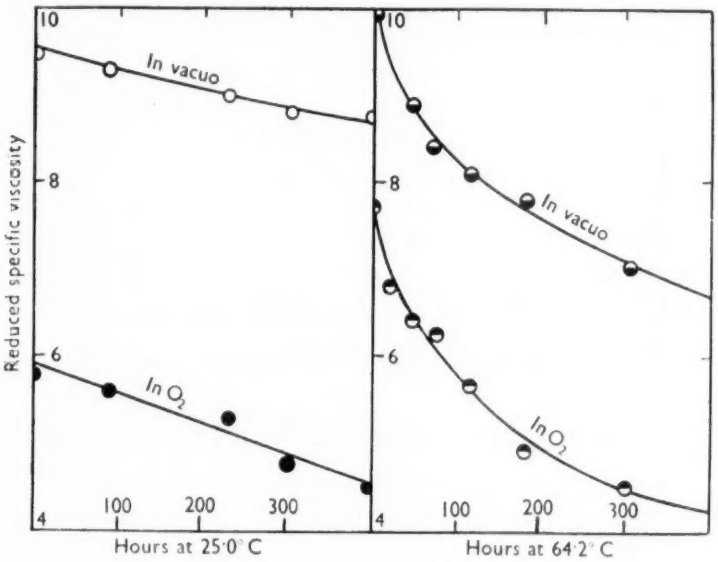


FIG. 3.—Degradation of 0·20 g. per 100 cc. smoked sheet in chlorobenzene *in vacuo* and 150 mm. Hg of oxygen at 25.0° and 64.2° C.

Since oxygen at a pressure of 10^{-2} mm. Hg did not detectably influence the rate of degradation, the relative rates of the nonoxidative degradation and degradation in the presence of oxygen at normal atmospheric pressures were measured at 25.0° and 64.2 C. The viscosity measurements show conclusively (Figure 3) that the greater part of the degradation of unpurified rubber in solution is by the nonoxidative scission process under normal conditions of storage. In marked contrast, oxidative scission is predominant when the rubber is highly purified; for example, fractionated rubber of initial reduced-specific-viscosity of 6.3 at 0.267 grams per 100 cc. in chlorobenzene decreased to almost a constant viscosity of 3.6 in 20 hours at 120° C, whereas it decreased to 0.08 in the same period in the presence of 150 mm. oxygen.

Influence of the concentration of rubber on the rate of degradation.—Four concentrations from the same stock solution of purified rubber in chlorobenzene were kept in vacuum viscometers at the same temperature (Figure 4). In-

spection of Figure 4 indicates that the relative rate of degradation was independent of the rubber concentration, which denotes a first-order dependence of rate on rubber concentration. This is supported by taking the intersections of these curves with lines parallel to the ordinate and thereby obtaining within experimental error linear plots of η_{sp}/c *vs.* c. Similar experiments with other grades of rubber at 100° C also gave first-order dependence on rubber concentration.

The influence of rubber purity on rate of degradation.—The rapid change in curvature of the plot of reduced specific viscosity *vs.* time of reaction makes it difficult to compare directly the rates of degradation of rubber samples differing both in initial purity and viscosity. However, log $(\eta_{sp}/c - \eta_{sp,f}/c)$ was found empirically to vary directly with time of reaction after an initial few hours

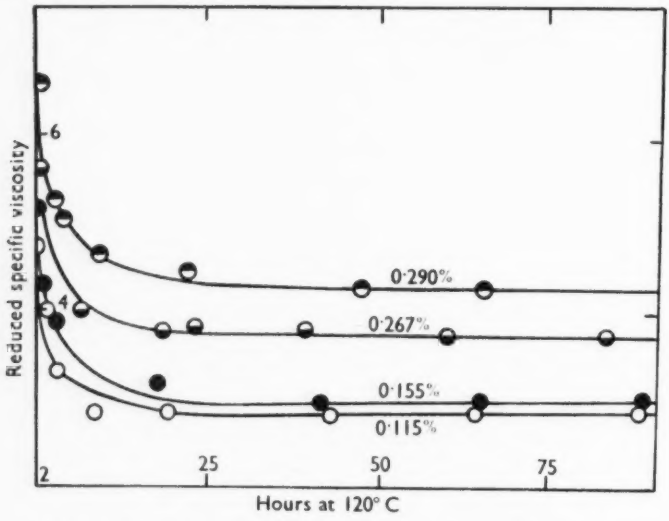


FIG. 4.—Degradation of purified rubber at several concentrations at 120° C.

degradation at 100° and 120° C for the rest of the measurable degradation. Considering the relationship between intrinsic viscosity and number-average molecular weight, $\eta = KM_n^a$, and the first-order dependence on rubber concentration, such a relationship is not unexpected. The slopes of the linear portions can then be considered as approximate measures of rates of degradation.

On expressing the results in this way, the series of linear plots for equal rubber concentrations against temperature were found to be of constant slope (*cf.* Figure 5). (The rubbers degraded at 120° C provide a particularly clear case owing to the fortuitous equal values of the ordinates at zero time), indicating that the rate of degradation was independent of the purity of the rubber.

Activation energy of degradation.—The conventional determination of the Arrhenius activation energy requires the velocity coefficients of the reaction at different temperatures to be known. It frequently happens, as here, that the reaction can be followed accurately by a change of a physical property of the

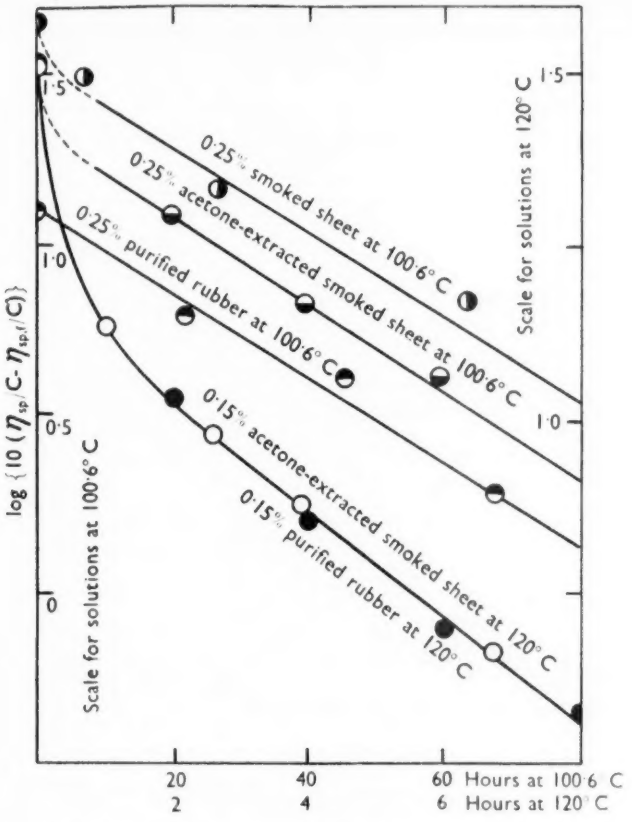


FIG. 5.—Degradation of rubber of different purity in chlorobenzene *in vacuo* at 100.6° and 120° C.

system, but that this property is an unknown function of extent of reaction. In the present case the velocity coefficients of degradation can be determined only from number-average molecular weights, with the unavoidable large experimental error involved. The following procedure utilizes any property of the system which varies in a single-valued manner with extent of reactions.

For rate expressions of the form $dX/dt = k[A]^a[B]^b[C]^c$ (1)

$$\int_1^{X_2} \frac{dX}{[A]^a[B]^b[C]^c} = k(t_2 - t_1) = k\Delta t \qquad (2)$$

where the products have increased from X_1 to X_2 in time t_1 to t_2. If it is arranged to carry out the reaction at two temperatures with the same values of the reactants over the same extent of reaction X_1 to X_2, the integral on the left-hand side of (2) must be identical for the two temperatures. Letting the

velocity coefficients be k' and k'' at the lower and higher temperatures and $\Delta t'$ and $\Delta t''$ be the periods for the same change from X_1 to X_2, then:

$$k'\Delta t' = k''\Delta t'' \tag{3}$$

Since $k = A \exp. - \Delta E/RT$,

$$\Delta E = R \frac{\int n(\Delta t'/\Delta t'')}{1/T_1 - 1/T_2} \tag{4}$$

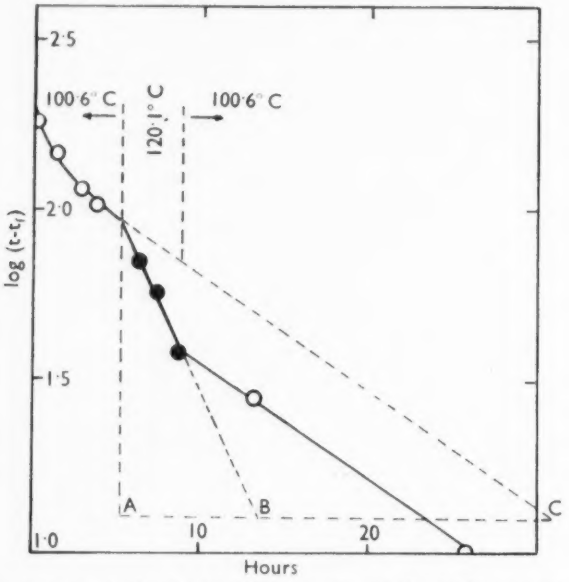


FIG. 6.—Determination of activation energy. Degradation of 0.25 g. per 100 cc. acetone-extracted smoked sheet at 100.6° and 120° C *in vacuo*.

TABLE 1

ACTIVATION ENERGY FOR THE DEGRADATION OF RUBBER *in vacuo* IN CHLOROBENZENE

Rubber purity	Concn. g./100 cc.	T_1 (° C)	T_2 (° C)	Δt	ΔE (kcal.)
Extracted smoked sheet	0.153*	100.0	120.0	3.15	16.8
Extracted smoked sheet	0.25*	100.6	120.1	2.9	15.9
Extracted smoked sheet	0.15	100.6	120.1	2.9	15.9
Extracted smoked sheet	0.25	100.6	120.1	3.0	16.5
Extracted smoked sheet	0.50	100.6	120.1	3.0	16.5
Extracted smoked sheet	0.25	100.6	120.1	2.85	15.7
Fractionally precipitated from crepe	0.25	100.6	120.2	3.0	15.8
Fractionally precipitated from crepe	0.50	89.0	110.5	3.3	15.3
Fractionally precipitated from crepe	1.00	89.0	110.5	3.1	14.8
Fractionally precipitated from Na alginate	0.25	89.0	110.5	3.3	15.3
Deproteinized coagulum	0.20	89.0	110.5	3.4	15.9

* Method using two viscometers.

The activation energy for degradation *in vacuo* was thus determined. Equality of specific viscosities on degradation at two temperatures gave the necessary equality of (unknown) X_1 and X_2, for which $\Delta t'$ and $\Delta t''$ were directly measurable. The use of two viscometers filled with the same stock solution and separately evacuated gave too divergent initial viscosities for accurate use of (4). Preliminary degassing of a common stock solution and filling of the two

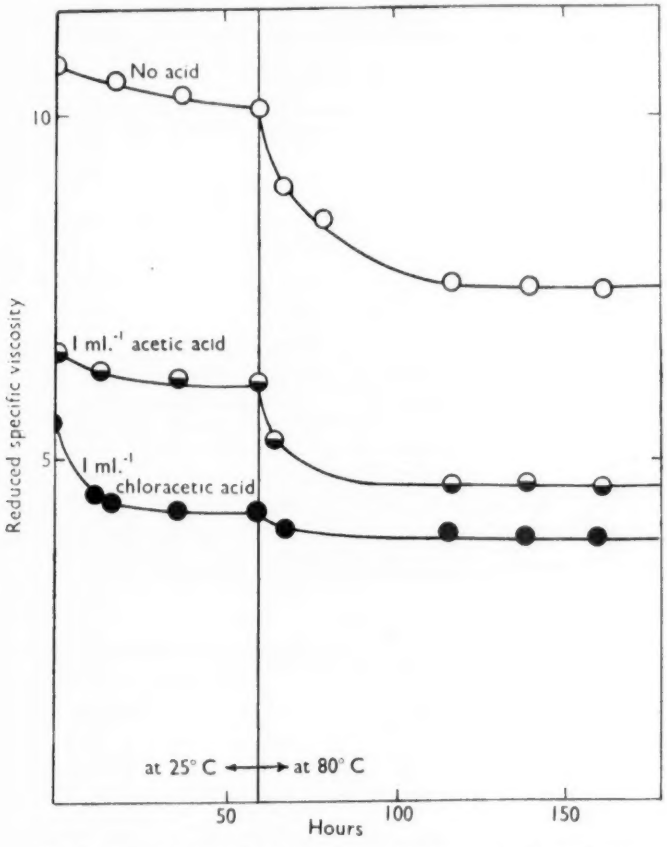


FIG. 7.—Degradation of 0.20 g. per 100 cc. smoked sheet in chlorobenzene with 1 cc.$^{-1}$ acetic and chloracetic acids.

viscometers *in vacuo* was satisfactory but laborious. The use of one viscometer containing the same evacuated solution was therefore adopted. The degradation was followed at the lower temperature till the linear portion of the log $(\eta_{sp}/c - \eta_{sp,f}/c)$ *vs.* t plot was reached, then followed over a period at the higher temperature, and finally again at the lower temperature (*cf.* Figure 6). In this way the extent of degradation which would have occurred at the lower temperature was obtained by linear extrapolation, and checked by parallelism with the third section. Then AC and AB gave respectively values for $\Delta t'$ and $\Delta t''$ for

substitution in (4). Activation energies so determined for extracted smoked sheet and rubber purified in different ways are summarized in Table 1. An average value for the activation energy of 15.9 ± 0.5 kcal. was obtained.

Effect of solvent.—Degradation proceeded similarly in chlorobenzene, tetralin, *n*-decane and nitrobenzene-chlorobenzene. The decrease to the constant limiting viscosity at 100° and 120° C was approximately at the same rate and independent of the purity of the rubber in these solvents.

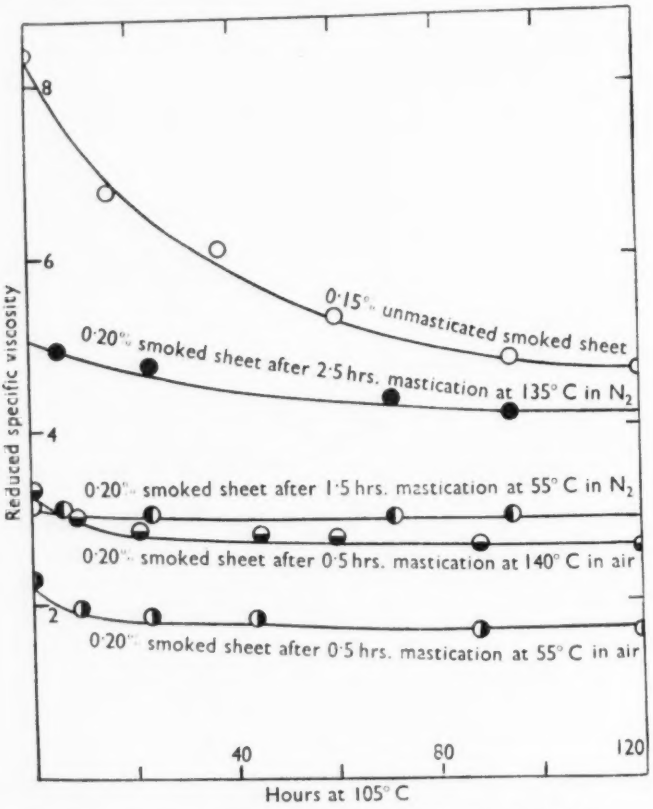

Reduced specific viscosity
8
6
4
2
0·15% unmasticated smoked sheet
0·20% smoked sheet after 2·5 hrs. mastication at 135° C in N2
0·20% smoked sheet after 1·5 hrs. mastication at 55° C in N2
0·20% smoked sheet after 0·5 hrs. mastication at 140° C in air
0·20% smoked sheet after 0·5 hrs. mastication at 55° C in air
40
80
120
Hours at 105° C

FIG. 8.—Influence of premastication on the degradation of smoked sheet in chlorobenzene at 105° C.

The rate of viscosity decrease was accelerated by addition of acids (Figure 7). Rubber in chlorobenzene with 1 cc.$^{-1}$ monochloracetic acid had almost reached the final reduced viscosity after 60 hours at 25° C, while it had undergone only the initial stages of degradation in the absence of acid. Consistently, the limiting viscosity was attained more rapidly at 80° C with the acid present. Acetic acid accelerated the degradation to a less marked degree. Trichloroacetic acid at 1 cc.$^{-1}$ caused an anomalous initial rise and then a slow viscosity at 25° C, but a rapid decrease almost to the viscosity of the solvent at 80° C.

Effect of premastication.—Samples of smoked sheet were masticated in a Banbury internal mixer (size B) in atmospheres of air and of nitrogen under cold and hot mastication conditions[3]. Viscosity measurements in chlorobenzene showed that cold mastication in air and nitrogen greatly reduced the subsequent degradation *in vacuo* (Figure 8). Hot mastication for an equal period was less effective in reducing the subsequent degradation, the reduction being of the order expected for degradation of rubber at these temperatures. Intrinsic viscosities before and after degradation (Table 2) confirm this reduction in extent of vacuum degradation after mastication.

TABLE 2

INTRINSIC VISCOSITIES OF MASTICATED RUBBERS BEFORE AND AFTER DEGRADATION AT 105° C

Mastication conditions	Intrinsic viscosity	
	Initial	Final
Unmasticated	5.20	3.24
85 minutes at 35° C in nitrogen	2.65	2.42
35 minutes at 55° C in air	1.86	1.42
150 minutes at 135° C in nitrogen	3.75	3.00
30 minutes at 140° C in air	2.38	1.76

Pregelling.—Some preliminary experiments have been carried out to ascertain if degradation *in vacuo* in solution is related to gel formation in stored rubber[4]. The gelling of rubber samples was accelerated by keeping at 100° C *in vacuo* in absence of water vapor. After different extents of gelling, the soluble rubber was extracted by leaving at room temperature in chlorobenzene for 5 days and the gel removed by passing under gravity through a Grade 2 sintered disc. The filtrates were then degraded *in vacuo* at 100° C in viscometers.

The gelling occurred at a comparable rate to degradation in solution at the same temperature (Table 3). The soluble rubber fractions all required the

TABLE 3

DEGRADATION OF RUBBER *in vacuo* AT 105° C AFTER GELLING

Hours at 100° C for gelling	% Gel	Intrinsic viscosity	
		Initial	Final
0	0	5.20	3.24
18	3	5.87	3.57
66	6	5.60	4.20
100	9	5.45	4.17

same time to attain the final viscosities quoted. Comparison of initial and final intrinsic viscosities shows that the amount of subsequent degradation of the soluble rubber was progresively reduced by gelling.

DISCUSSION

The only explanation which appears to account for the degradation *in vacuo* is that the rubber contains occasional weak bonds, which undergo irreversible scission on maintaining the rubber in solution. The difficulty in obtaining positive proof for the existence of weak bonds demands that this hypothesis be advanced with caution, but the low activation energy of degradation, first-

order dependence on rubber concentration, and final production of a rubber of constant viscosity seem to admit of no other explanation. The decreased degradation after cold mastication is also difficult to interpret as other than rupture of weak bonds by the applied shearing forces. The independence of rate of degradation on rubber purity is evidence that the postulated weak links are an integral part of the structure of the polymer. Also, the constancy of rate of degradation for given weights of rubber of different average chain lengths suggests that there are a fixed number of these links for a given number of monomer units.

This number can be readily calculated from the value of initial and final molecular weights. The results support the expected constancy of weak link concentration for rubbers of different molecular weight, origin and purity (Table 2). A concentration of one weak link per 1.3×10^4 monomer units is obtained. The number from the osmotically-determined molecular weights is the fundamental one in so far as experimental accuracy allows. Intrinsic viscosities have been converted to molecular weights by the relation $\eta = 10^{-5} M_n^{0.98}$. This relation was empirically obtained from data on molecular weights and intrinsic viscosities of masticated rubbers[5]. Since thermal degradation is

TABLE 4

CONCENTRATION OF WEAK LINKS FROM OSMOTIC AND VISCOMETRIC MOLECULAR WEIGHTS

Rubber	T °C	$M_{n,i} \times 10^{-5}$	$M_{n,f} \times 10^{-5}$	No. of monomer units / No. of weak links $\times 10^{-4}$
Smoked sheet	99.4	25.0*	6.7*	1.3
Purified rubber	100.0	2.75	2.03	1.2
Purified rubber	120.0	3.6	2.6	1.4
Extracted smoked sheet	100.0	5.2	3.3	1.3

* Determined osmotically.

also a random degradation process, the same relationship is expected to hold as for masticated rubber, and is to be preferred to that applying for fractionated rubbers[6].

A commercially important property of natural rubber is the formation of a cross-linked fraction on storage, accounting for up to 80 per cent of the rubber. Gel formation has some features similar to degradation in solution *in vacuo*; (1) it is a nonoxidative process; (2) it probably has a low activation energy, since it occurs at a measurable rate in a few days at room temperature[4]; (3) gelation and degradation occur at comparable rates at 100° C; (4) the degree of cross-linking is of the order of one cross-link per 8×10^3 monomer units[7]. The reduced degradation after gelling means that the potential degrading centers of the soluble rubber are reduced on gelling. This would occur if these centers of cross-linking and gelling were the same or if degradation was occurring independently under gelling conditions. Gel formation and vacuum degradation thus appear to be associated processes, their difference in effect being due to cross-linking and degradation proceeding with different facility in solid rubber and solution. The occurrence of weak links in rubber hydrocarbon has an obvious biochemical significance, and, if established, serves to parallel the rare weak linkages found in other natural high polymers.

This work forms part of the program of research of the British Rubber Producers' Research Association.

SUMMARY

Rubber in solution degrades in the absence of oxygen. This nonoxidative degradation is the main cause of the decrease of viscosity of rubber solutions on storage. The rate of degradation is proportional to the rubber concentration and is independent of the purity and molecular weight of the rubber initially. The energy of activation for degradation in chlorobenzene is 15.9 $\pm$ 0.5 kcal. The rate of reaction is not influenced by different nonpolar solvents for rubber, but is accelerated by acids. These results suggest that rubber polymer possesses one anomalous bond per 1.3×10^4 monomer units. Evidence is advanced for this phenomenon being associated with the gelling of solid rubber on storage.

REFERENCES

[1] Bolland, *Quart. Rev.* **1**, 3 (1949).
[2] Bolland and ten Have, *Faraday Soc. Discussion* No. 2, **1947**, p. 252.
[3] Pike and Watson, *J. Polymer Sci.* **9**, 224 (1952).
[4] Wood, *J. Rubber Research Inst. Malaya* **14**, No. 279 (1952).
[5] Stern, J., and Freeman, R., unpublished results.
[6] Carter and Scott, *J. Am. Chem. Soc.* **68**, 1480 (1946).
[7] Flory, *J. Phys. Chem.* **46**, 132 (1942).

STRUCTURE AND PROPERTIES OF LOADED RUBBER MIXTURES. IX. MODIFICATION OF CARBON STRUCTURES BY REPEATED DEFORMATIONS *

K. Pechkovskaya, Ts. Mil'man, and B. Dogadkin

Scientific Research Institute of the Rubber Industry, Moscow, USSR

In preceding papers[1] the presence of a network structure of active fillers in raw and vulcanized rubbers and the influence of this structure on the properties of the vulcanizates were described. The degree of development of carbon black structures is measured by the specific resistivity ρ of the rubber; the greater is ρ, the smaller is the degree of development of the carbon black structures.

However, the structures of various carbon blacks differ not only in the degree of development, but also in the nature of the contact between the carbon particles. In the case of channel carbon black, this is chiefly direct contact of the particles, although in contact with some particles there is an intermediate layer of rubber or some other ingredient in the mixture which does not conduct a direct electric current. The number of these particles is much larger in the other carbon blacks studied than in channel carbon black. The prevailing type of contact was determined by the relation between the amperage of the current passing through the test-specimen and the applied voltage. A linear or approximately linear relation, according to Ohm's law, indicates that direct contact between the carbon black particles prevails. A sharp deviation from a linear relation indicates a second, non-ohmic conductivity mechanism, due to the presence of dielectric layers in the path of the electric current.

Analysis of the voltage-amperage curves showed that the relation of the strength of a current to the voltage corresponds satisfactorily to the equation: $I = C \cdot V^n$; where I is the energy of the current in amperes passing through a unit length and cross-section of the specimen; V is the stress in volts, and C and n are constants.

With logarithmic coordinates, the experimental points give satisfactory curves (see Figure 1).

If the second (non-ohmic) mechanism of flow is absent or its role is extremely small, then the coefficient is $n \approx 1$. The greater is the deviation of this factor from 1, the greater is the part played by the second mechanism of flow and, consequently, the greater is the matrix of non-conductive matter in the structure formed by the particular carbon black in the rubber mixture.

The degree of structure development and the nature of the prevailing contact depend on the type of rubber used as well as on the type of carbon black added to it. This can be illustrated by the curves in Figure 1, which show the electric properties of mixtures of sodium-butadiene rubber containing three different types of carbon black. These curves differ, in the first place, by their position with respect to the coordinates (the curve for channel carbon is located

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Kolloidnyi Zhurnal* (*Colloid Journal*), Vol. 14, No. 4, pages 250–259 (1952).

in a region of much greater conductivity than the other two curves), and, in the second place, in the tangent of the slope of the curves; that is, the coefficient n is much smaller in the case of channel carbon black.

The degree of development of the ρ structure and the nature of the prevailing contact n are not the only differences, however, between various types of carbon blacks. The strength of the bond between the particles in the carbon black structures is also a characteristic property. This property can be determined by studying the behavior of various carbon black structures under various conditions of mechanical stress and of temperature.

In the works of other authors, relatively little has been written on this question. A number of investigators[2], studying the properties of electrically conductive rubbers, showed that the specific resistivity ρ increases during stretching and approaches a definite limit. This appears to be due to gradual destruction of the carbon chains during stretching. Other investigators[3], confirming the increase of electric resistivity of rubber-carbon black mixtures dur-

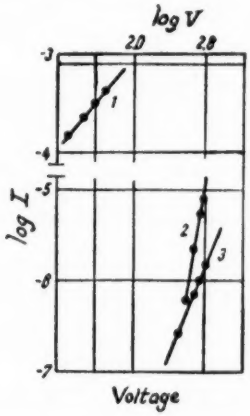


FIG. 1.—Relation of current amperage to voltage for rubber containing different types of carbon black. 1. Channel. 2. Nozzle. 3. Furnace.

ing elongation, also observed an exponential decrease of this factor with time at constant elongation. The latter phenomenon indicates a gradual restoration of the carbon black structures which were destroyed during stretching.

Besides changing the electric resistivity, stretching modifies other properties of rubber-carbon black mixtures[4], for example, their hardness.

In this work, problems connected with the behavior of carbon black structures during mechanical treatment of rubber mixtures are discussed; the behavior of these structures in relation to temperature changes and the restoration of the destroyed structures in the relaxation of rubber will be treated in a later study.

EXPERIMENTAL PART

Influence of the type of rubber on the degree of development of carbon black structures.—We observed above that the degree of development of carbon black structures depends on the type of rubber used. Table 1 shows values of ρ and n for various vulcanized rubbers, each containing 50 parts by weight of channel carbon black per 100 parts of rubber.

It is clear that the most highly developed carbon black structures are formed in Butyl rubber and in natural rubber; that is, in rubbers with high degrees of crystallization, caused by the regularity of the structure of their molecules. The carbon black structure develops least in butadiene-styrene rubber[5], which possesses a more complicated molecule in comparison with the others listed in the table. In this series, the sodium-butadiene rubbers occupy an intermediate position. That the nature of distribution of carbon blacks in the rubbers is related to their molecular structure is confirmed to some extent by the curves

TABLE 1

ELECTRICAL CHARACTERISTICS OF VARIOUS RUBBERS

Type of rubber	ρ (ohm-cm.)	n
Butyl rubber	1.9×10^3	1.00
Kok-saghyz	7.7×10^3	1.01
Smoked sheet	5.5×10^4	1.11
Unloaded sodium-butadiene rubber	7.5×10^4	1.18
Loaded sodium-butadiene rubber	2.1×10^5	1.15
Butadiene-styrene copolymer (Buna S-4)	1.1×10^6	1.35

in Figure 2, which shows the voltage-amperage characteristics of vulcanizates of Buna S-3, plasticized by various methods, and containing different proportions of carbon black.

In the case of a plasticized rubber prepared by mastication on a cold mill, the carbon structure is considerably more developed than in the case of the same rubber plasticized on a hot mill, although the plasticity in both cases is roughly the same (0.407 and 0.415).

As Betz and Karmin[6] have shown, heat plasticization of a butadiene polymer gives products which possess a much more complex molecular structure than

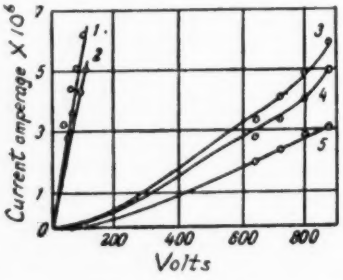


FIG. 2.—Relation of current amperage to voltage for different plasticized mixtures. 1. Cold (plasticity 0.407). 2. Unplasticized rubber. 3, 4, and 5. Heat-plasticized (plasticity—0.421, 0.415, 0.308).

those obtained by the cold method. The surface-active agents which are present in the rubber and which aid in the dispersion of carbon black also play an obviously important part. This is seen, for example, by a comparison of two natural rubbers, kok-saghyz and smoked sheet, in the first of which the surface-active resins are present in much higher percentage than in the second. One sees from Table 1 that vulcanized kok-saghyz rubber has a much lower specific resistivity ρ, and consequently, a more highly developed carbon structure, than vulcanized smoked sheet containing the same proportion of carbon black.

Influence of the type of carbon black on the degree of development of carbon structures.—The type of carbon black has an even greater importance in the development of structure than does the type of rubber. Table 2 gives the values of ρ and n for vulcanizates of kok-saghyz rubber containing different types of carbon blacks.

As one would expect, the results conform well to the mean diameter of the particles of carbon black studied; the smaller this diameter, the greater the number of particles which can take part in the structure formation at equal-weight concentrations. However, the observed differences in the factors ρ and n are caused, not only by the dispersivity of the carbon blacks, but also by their other properties, which will be discussed later.

Change of carbon structures by stretching and recovery.—In the deformation of vulcanized rubber containing carbon black, stresses arise in the cross-links of the carbon network which, reaching a definite critical value, cause these links to rupture. As deformation increases, the critical stresses all develop in the new links, destroying them, and leading to an increase of electric resistivity ρ of the test-specimens. The carbon structure hardly ever forms entirely as a result

TABLE 2

ELECTRICAL PROPERTIES OF RUBBERS CONTAINING DIFFERENT CARBON BLACKS

Type of carbon black	Carbon black content in parts by weight per 100 parts of rubber	ρ (ohm-cm.)	n	Mean diameter of carbon black particles ($m\mu$)
Channel carbon black	40	5.5×10^4	1.07	26
	50	7.7×10^3	1.01	26
	60	6.0×10^2	1.00	26
Furnace black (Kosmos-40)	60	3.1×10^2	1.02	41
Lampblack	60	1.0×10^4	1.26	140
Thermal black	60	2.7×10^4	1.32	210
Furnace black	100	$>1.0 \times 10^9$	—	600

of the carbon-carbon bonds; it contains a varying quantity (depending on the type of rubber and carbon black) of links associated with the rubber-carbon bonds. Depending on which of these bonds in the given vulcanizate is stronger, deformation will cause a decrease of the proportion of bonds of one type and a corresponding increase of the proportion of bonds of the other type. Rupture of the rubber-carbon bonds is reflected in the approach of the coefficient to unity, since the proportion of carbon-carbon bonds increases. Conversely, rupture of the carbon-carbon bonds causes an increase of this factor, since the proportion of nonconductive layer is increased.

Our results show that stretching causes an increase of the value of ρ of the specimen only up to a certain elongation, depending on the composition of the test-specimen and its dimensions. At higher elongations, a decrease of the value of the test-specimen is observed. In summation, the change of ρ with elongation in the first deformation cycle is expressed by a curve with a maximum, which for some types of vulcanizates is not very pronounced. Figure 3 shows this curve for vulcanized smoked sheet containing 50 parts by weight of carbon black (curve 1, continuous line). The highest value of ρ in this case is at an elongation of about 70 per cent. The similar nature of the dependence of

ρ on the elongation attests to a simultaneous development of two opposingly directed processes, the combined effects of which result in this shape of curve. The first of these processes is the above-mentioned destruction of the separate links of the carbon structure, in which the stress reaches a critical value, causing an increase of ρ of the test-specimen. The second process, or group of processes, consists in the orientation of the elements of the carbon structure in the direction of stretching, causing an increase of the number of conductive paths in a cross-section of the test-specimen, and, consequently, a decrease of ρ; in addition, new contacts with increasing time are formed, and these lead to a further decrease of ρ of the test-specimen. In the beginning of the cycle the first process prevails; however, as deformation develops the number of links of the carbon structure subject to rupture under the given conditions becomes smaller and the number of orienting elements or the degree of their orientation becomes larger. As a result, at a definite elongation, the latter processes prevail, and the ρ value

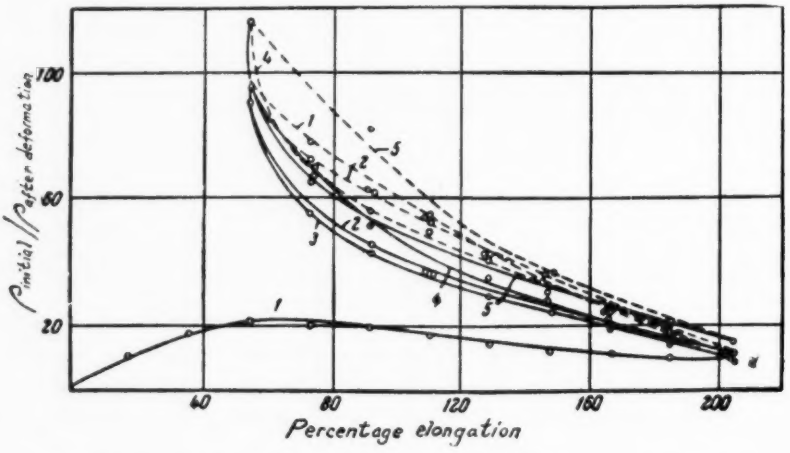


FIG. 3.—Modification of carbon structure in initial cycles; stretching (continuous line); recovery (dotted line). The figures on the curves indicate the sequence of cycles of deformation.

of the test-specimen begins to decrease. Recovery after stress of the specimen leads to instantaneous destruction of the orientation (a destruction of the time contacts), while restoration of the destroyed links requires a much longer time. Therefore, the ρ value of the test-specimen during recovery sharply increases, reaching a value many times greater than the maximum on the curve of the first cycle of stretching (see Figure 3, dotted line 1). The second cycle of stretching depends principally on the orientation process, since the number of newly destroyed links is still negligible; consequently, during secondary stretching, the ρ value of the test-specimen decreases abruptly and reaches values close to the final value of ρ in the first cycle of stretching (see Figure 3, curve 2, continuous line). Secondary recovery again leads to a sharp increase of ρ, also due to destruction of the orientation (see Figure 3, curve 2, continuous line). Subsequent stretching-recovery cycles add only slightly to the number of destroyed links, so the final values of ρ (at 200 per cent elongation) lie very close to each other (see Figure 3, curves 3, 4, and 5).

Thus, in the deformation of rubber-carbon black vulcanizates, there is not only rupture of a certain proportion of the links of the carbon structure, but also other processes caused by the change of the relative distribution of the undestroyed elements of this structure. It was of interest to explain the nature of the relation of the elongation to this part of the change of ρ which depends only on the rupture process. With this in mind, a test-specimen stretched to a given elongation was allowed to recover and ρ was measured both immediately and 30 minutes after recovery. The results are shown graphically in Figure 4. In this case the degree of destruction of the carbon structure increases with elongation (within the limits of the values of elongation studied), as one would expect, after discounting the effects of orientation. The rate of restoration of the destroyed structure increases simultaneously, since the 30-minute relaxation of the specimen causes a decrease of ρ proportional to the elongation of the stretched test-specimen.

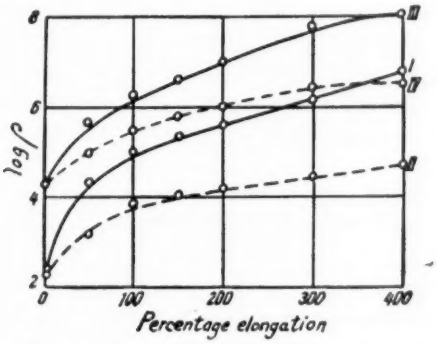


FIG. 4.—Relation of value of ρ to deformation time imediately after recovery (continuous line) and 30 minutes after recovery (dotted line): I and II—rubber containing nozzle carbon black. III and IV—rubber containing channel carbon black.

The curves of Figure 4 represent two types of vulcanized kok-saghyz rubber; one of these contains nozzle carbon black (curves I and II), the other, channel carbon black (curves III and IV). Comparison of these curves discloses that at small elongations (up to 50 per cent), destruction of the carbon structure is more effective in the case of nozzle carbon black, as indicated by the steeper slope of curves I and II at this point.

Modification of carbon structures during repeated deformations.—The same two series of test-specimens, that is, the various vulcanizates containing 50 parts by weight of channel carbon black, and the kok-saghyz vulcanizates containing various carbon blacks, were subjected to repeated deformations.

Test-specimens were stretched repeatedly on a de Mattia machine at a frequency of 500 cycles per minute and amplitude of deformation of 50 per cent, for 10 minutes and 12 hours. The electrical properties were measured before and after fatiguing. The results are shown in Tables 3 and 4.

The stability index of the carbon structure, listed in the next to the last column of each table, gives the conventional values of the part of the structure not destroyed during deformation, and equal to:

$$\frac{\log \rho \text{ before fatigue}}{\log \rho \text{ after fatigue}}$$

This index depends only to a slight degree on the type of rubber and carbon black, but principally on the percentage of carbon black in the rubber, decreasing as the loading increases (Table 4).

The change of the coefficient n depends more on the type of carbon black than on the type of rubber. In fact, all the specimens containing channel carbon black, regardless of the type of rubber and percentage of carbon in the

TABLE 3

ELECTRIC PROPERTIES OF RUBBERS BEFORE AND AFTER FATIGUE

	Before fatigue		After 10 minutes of fatigue		After 12 hours of fatigue		Stability index of structure in %		
	ρ (ohm-cm.)	n_0	ρ (ohm-cm.)	n_1	ρ (ohm-cm.)	n_2	After 10 minutes' fatigue	After 12 hours' fatigue	$\frac{n_0}{n_1}$
Butyl rubber	1.9×10^9	1.00	5.5×10^9	1.00	7.7×10^9	1.00	88	84	1.00
Kok-saghyz rubber	7.7×10^9	1.01	4.7×10^9	1.00	—	—	83	—	1.01
Smoked sheet rubber	5.5×10^9	1.11	3.0×15^8	1.00	1.7×10^6	1.00	87	76	1.11
Sodium-butadiene rubber (unloaded)	7.5×10^9	1.18	1.1×10^6	1.00	5.2×10^6	1.00	81	73	1.18
Sodium-butadiene rubber (loaded)	2.1×10^5	1.15	6.2×10^6	1.00	9.7×10^6	1.00	78	76	1.15
Buna (S-4)	1.1×10^6	1.35	—	—	4.2×10^7	1.14	—	79	—

mixture, show a decrease of the coefficient n after repeated deformations in those cases where this coefficient was greater than unity. Consequently, in these test-specimens, deformation causes destruction of the carbon structure chiefly in the cross-linkages of the rubber-carbon bonds; as a result, the proportion of carbon-carbon bonds in the whole structure increases. Furthermore, since destruction is more widespread among the weaker links, in vulcanizates con-

TABLE 4

ELECTRIC PROPERTIES OF RUBBER CONTAINING DIFFERENT CARBON BLACKS BEFORE AND AFTER FATIGUE

Type of carbon black	Carbon black content in parts by weight per 100 parts rubber	Before fatigue		After 10 minutes' fatigue		Stability index (%)	$\frac{n_0}{n}$
		ρ (ohm-cm.)	n_0	ρ (ohm-cm.)	n		
Channel	40	5.5×10^4	1.07	1.4×10	1.00	92	1.07
	50	7.7×10^3	1.01	4.7×10^4	1.00	83	1.01
Furnace (Kosmos-40)	60	6.0×10^2	1.00	5.4×10^2	1.00	75	1.00
Furnace (Kosmos-49)	60	3.1×10^2	1.02	1.3×10^3	1.02	80	1.00
Nozzle	60	1.0×10^4	1.26	1.3×10^5	1.42	78	0.88
Lampblack	60	2.7×10^4	1.32	1.5×10	1.79	85	0.74

taining channel carbon black, the carbon-carbon bonds proves stronger than the rubber-carbon bond.

In the case of furnace carbon black, deformation does not change the value of the coefficient n; consequently in such rubber mixtures, the rubber-carbon and carbon-carbon bonds are practically equivalent. Finally, deformation of vulcanizates containing nozzle carbon black or lampblack causes a sharp increase of the coefficient n; it follows that in these rubbers the carbon-

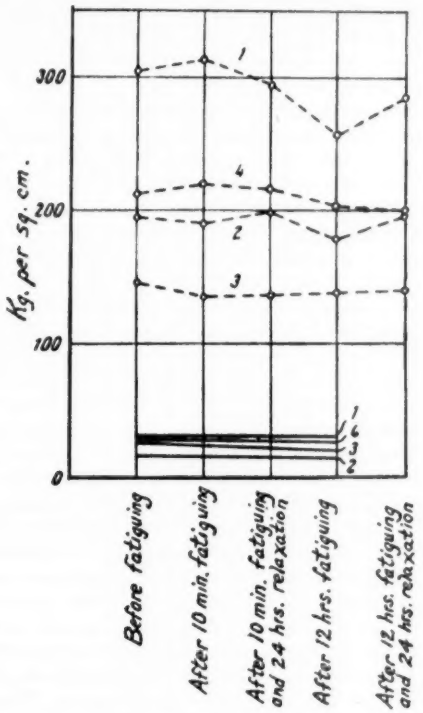


FIG. 5.—Effect of fatigue on properties of vulcanizates of four elastomers (continuous line indicates stress at 100 per cent elongation; dotted line, tensile strength): 1. Smoked sheet rubber. 2. Butyl rubber. 3. Sodium-butadiene rubber. 4. Buna S-3.

carbon bonds are weaker than the rubber-carbon bonds. Of primary importance is the fact that the carbon blacks studied follow the same order when classified according to the strengths of the bonds between the particles (intermolecular bond) than they do when classified according to their reinforcing effects.

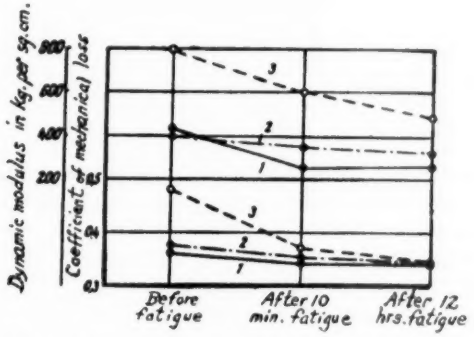


FIG. 6.—Effect of fatigue on loss of mechanical properties of different vulcanizates: 1. Sodium-butadiene rubber. 2. Smoked sheet rubber. 3. Buna S-3.

INTERPRETATION OF THE RESULTS

Electron-microscope studies showed that all the carbon-blacks in powdered form tend to form small-chain structures, which are maintained to some degree even after the blacks have been incorporated in rubber. However, as was shown above, the nature of these structures (the principal form of contact and the strength of the bond between the particles) differs for various carbon blacks. This difference can be observed in the experimental data presented above; for example, the much higher resistance to mechanical stress observed with channel carbon black chains in comparison with chains of the other carbon blacks studied. Naturally one wonders what structural peculiarities or properties of channel carbon black are responsible for the greater mechanical "strength" of the bond between its particles. These properties may be related to the structure of the carbon particles, to the presence of active particles on its surface, or to the composition of the layer adsorbed on the surface of the particles. Information concerning this process can be obtained from the scientific literature.

For example, measurements of the differential heats of adsorption of various substances have revealed on the surface of reinforcing carbon blacks the presence of segments with a higher energy, in which adsorption takes place first and with a greater heat effect (15–20 kcal. per g.-mol.)[7]. These active segments can be regarded as the points of emergence on the surface of particles of the ends of parallel distributed groups (crystallites) formed by the graphite-like layers, and constituting, as is known, the structural elements of the carbon particles. The ends and especially the angles of these crystallites possess more energy because of the unsaturation of their end carbon atoms due to the distribution of these atoms in the plane of the graphite-like layers. The simplest explanation of the greater energy of these particles in the case of channel carbon blacks (in comparison with others) would be the difference in the distance between the planes of the parallel groups of the various carbon blacks. However, all previous x-ray measurements[8] have indicated that the distance between the planes in most carbon blacks is approximately the same, and varies between 3.53 and 3.57 Å; an exception is acetylene carbon black, in which this distance is smaller than in the others (3.47 Å) and close to the value for graphite (3.35 Å). However, the potentialities of x-ray analysis are by no means exhausted; use of more accurate methods may provide more accurate results in the measurement of the distance between planes in carbon crystallites.

Different processes of carbon formation which occur during the preparation of carbon blacks by various methods can cause differences of the density of the crystallite packing of the particles and different types of orientation. The loosest packing was observed in particles of acetylene black by measuring the real and apparent density in liquid helium and in substances of coarser molecules.[9] As with the other carbon blacks, the varying density of the crystallite packing in their molecules was not detected, even by this relatively accurate method.

Differences of the type of orientation of the crystallites have been observed in the investigation of carbon blacks by means of a dark electron microscope[12]. This investigation showed that in the particles of inactive and only slightly active carbon blacks, the crystallites in the surface layer are mostly oriented parallel to the surface of the particle. In channel carbon blacks, no such orientation was observed. Consequently, in this case the orientation of the crystallites can be regarded as perpendicular to the surface or at some angle to it; in both cases ends or edges and angles of the crystallites emerge on some of

the surface segments, which thereby acquire a higher energy. Collision of the carbon particles with these segments can cause the formation of stronger bonds than by the ordinary van der Waals reaction.

The layer of substances adsorbed on the surface of the carbon particles may also be of great importance. The channel black process makes possible oxidation reactions on the surface of the particles, as a result of which the substances adsorbed by channel carbon black may contain a large number of functional groups. This too may be one of the causes of the formation of a stronger bond (particularly a hydrogen type bond) between the particles of channel carbon black than between the particles of the other carbon blacks studied.

Consequently there is sufficient reason to believe that the energy of reaction of carbon black particles during chain formation in the case of channel carbon black is greater than in the case of other carbon blacks (excluding acetylene black). It is extremely significant that the carbon blacks studied fall into the same order according to resistance to mechanical stresses (the best index of this resistance is the relation n_0/n, presented in Tables 3 and 4) as when arranged according to their reinforcing effects in rubber. This once again supports our hypothesis that the structure formation in rubber mixtures is one of the principal factors of the reinforcing action of carbon blacks in rubber. On the other hand, the inevitable destruction of part of the carbon structures during repeated deformations, and also the ensuing orientation and disorientation of the elements of the carbon structures causes heat build-up; the more, the greater the amount of work expended in permanent destruction and displacement. From this it is clear that the weaker structures of nozzle black and lamp black require much less work for this destruction than the stronger structures of furnace black, and especially, channel carbon black. Consequently, the heat build-up in rubbers containing nozzle or lamp black must also be less than in rubbers containing channel carbon black, and this accords completely with the experimental data.

CONCLUSIONS

1. The structure of the carbon black phase of a rubber-carbon black vulcanizate is characterized first of all by a specific number of rubber-carbon black and carbon black-carbon black bonds (or contacts) and, in turn, by a specific proportion of these two types of bond.

2. The total number of bonds in the carbon structure, or the degree of their development, is indicated by the specific electric resistivity ρ of the vulcanizate, which decreases with the development of this structure.

3. Measurement of the proportion of carbon-carbon bonds in the structure establishes the factor n of the equation $I = CV^n$, relating the energy of the current which flows through the test-specimen to the constant by the difference of the potentials. If $n = 1$, all the bonds in the carbon structure which take part in the transmission of the current are of the carbon-carbon type, and the rubber mixture possesses a purely ohmic conductivity; in all other cases $n > 1$.

4. During the deformation of loaded vulcanizates, changes of the specific resistivity ρ, and also of the factor n, take place. In the first cycle of stretching, ρ at first increases and then decreases slightly. During recovery after stressing, the electric resistivity sharply increases, reaching after the stress is removed a value several times greater than the maximum on the ρ curve of the first cycle of deformation. In succeeding deformation cycles, the change of resistivity proceeds with relatively slight hysteresis effects.

5. In the deformation of loaded rubbers, the weaker bonds are largely destroyed, and consequently the proportion of bonds of the stronger type increases. In cases where the carbon-carbon bonds are stronger than the rubber-carbon bonds, the value of n after deformation is smaller than that of n_0 before deformation, or $n_0/n > 1$; in the opposite case, $n_0/n < 1$.

6. Both parameters (n and ρ) depend on the type of rubber; their greatest values, corresponding to a less developed structure with a small proportion of carbon-carbon bonds, are observed in the case of butadiene-styrene rubber; in sodium-butadiene rubbers, the degree of structural development and proportion of carbon-carbon bonds are much higher; the most highly developed carbon structure and the greatest proportion of carbon-carbon bonds are found in Butyl and natural rubbers. Hence, the value of n_0/n is hardly related to the type of rubber.

7. Both parameters also depend on the type of carbon black. The most highly developed structures, with a large proportion of carbon-carbon bonds, are observed with channel carbon black, where these bonds are stronger than the rubber-carbon bonds, *i.e.*, $n_0/n > 1$. The least developed structure, with a small proportion of carbon-carbon bonds, is observed with nozzle black and lampblack, in which cases these bonds are weaker than the rubber-carbon bonds, *i.e.*, $n_0/n < 1$. Furnace blacks occupy an intermediate position. Thus, the carbon blacks studied are classified according to the value of n and the relation n_0/n in the same sequence as when classified according to their reinforcing effects. The possible causes of this distribution are discussed.

8. The great strength of the bond between the particles of more active (channel) carbon blacks is one of the reasons for the greater heat formation in rubbers containing these carbons. Heat formation in rubbers containing less active carbon blacks (nozzle black, lamp black) which possess a weaker bond between their particles when all other conditions are equal, is much less.

REFERENCES

[1] Dogadkin, Pechkovskaya, and Chernikina, *Kolloid. Zhur.* **8**, Nos. 1-2, 31 (1946); Dogadkin, Pechkovskaya, and Dashevaskil, *Kolloid. Zhur.* **10**, No. 5, 357 (1948); Dogadkin, Pechkovskaya, Semanovskaya, and Kupriyanova, "Study of the Physics and Chemistry of Rubbers", *Repts. Research Inst. Tire Ind.*, **1950**, p. 120.

[2] Bulgin, *Trans. Inst. Rubber Ind.*, **21**, 188 (1945).

[3] Wack, *J. Applied Physics* **18**, 456 (1947).

[4] Mullins, *Trans. Inst. Rubber Ind.* **23**, 280 (1948); *J. Phys. Colloid Chem.* **54**, 239 (1950); Blanchard and Parkinson, RUBBER CHEM. & TECHNOL. **23**, 615 (1950).

[5] Dogadkin, Pechkovskaya, Semanovskaya, and Kupriyanova, "Study of the Physics and Chemistry of Rubbers", *Repts. Research Inst. Tire Ind.*, **1950**, p. 120; Bulgin, *Trans. Inst. Rubber Ind.* **21**, 188 (1945).

[6] Karmin and Betz, *Repts. 6th Conf. High Molecular Compounds*, **1949**, p. 129.

[7] Smith, and Schaeffer, RUBBER CHEM. & TECHNOL. **23**, 625 (1950); Schaeffer, *J. Phys. Colloid Chem.* **54**, 227 (1950).

[8] Clark, Eckert, and Burton, *Ind. Eng. Chem.* **41**, 201 (1949); Arnell and Barss, *Can. J. Research* **26A**, 236 (1948).

[9] Rossman and Smith, *Ind. Eng. Chem.* **35**, 972 (1943).

[10] Hall, *J. Applied Physics* **19**, 271 (1948).

STRUCTURE AND PROPERTIES OF LOADED RUBBER MIXTURES. X. ALTERATION OF CARBON BLACK STRUCTURES BY HEAT TREATMENT *

B. A. Dogadkin, K. Pechkovskaya, and Ts. Mil'man

Institute of Fine Chemical Technology, Moscow, USSR

In the previous paper of this series[1] we discussed the alteration of the reticular structures formed by various carbon blacks in rubber mixtures as a result of repeated deformations. The results obtained showed that in the structures of relatively active carbon blacks (channel blacks) the carbon-carbon bonds are stronger than the rubber-carbon bonds; in the structures formed of less active carbon blacks (nozzle and lamp black) on the contrary, the rubber-carbon black bonds are stronger. The type of bonds as well as the nature of the distribution of carbon black in the rubber, determines to a large degree such important physical-mechanical properties of rubber as its tensile strength and heat build-up.

The relation of the carbon structures to the effect of higher temperatures is no less interesting. In earlier works[2], a study of several carbon blacks showed that the specific electric resistance ρ of rubber-carbon black mixtures changes exponentially with rise of temperature and that the sign of the temperature coefficient of electric resistance of these rubber mixtures varies. However, in these works such questions as the relation between the rubber-carbon and carbon-carbon bonds which are formed by the different carbon blacks in the structures, and the influence of the temperature of deformation and relaxation on the state of the carbon structures were not considered at all. Experimental material regarding these questions is provided below.

RELATION OF THE SPECIFIC ELECTRIC-RESISTIVITY ρ OF VULCANIZATES TO TEMPERATURE

We studied vulcanizates of kok-saghyz rubber containing 60 parts by weight of channel or nozzle black per 100 parts of rubber and vulcanized butadiene-styrene rubber with the same carbon-black concentration. Before ρ was measured, the specimen was kept at each temperature for 30 minutes. The change of log ρ of these vulcanizates during heating (see the curves in Figure 1) shows the existence of a linear relation in all three cases up to 100° C. Consequently, in this temperature interval the following equation is valid:

$$\rho_t = \rho_0 e^{\alpha t}$$

where ρ_t is the specific electric resistivity of the vulcanizate at t° C, ρ_0 is the same factor at 0° C, and α is a constant.

Table 1 gives the values of the coefficient α for the three systems studied.

* Translated for Rubber Chemistry & Technology by Alan Davis from the *Kolloidnyi Zhurnal*, Vol. 14, No. 5, pages 346–356 (1952).

TABLE 1

VALUE OF COEFFICIENT α FOR MIXTURES CONTAINING VARIOUS CARBON BLACKS

Type of rubber	Type of carbon black	
Kok-saghyz rubber	Channel black	−0.0096
Butadiene-styrene rubber	Channel black	−0.024
Kok-saghyz rubber	Nozzle black	+0.0107

As is evident, the sign of the coefficient α differs for the two carbon blacks studied; in other words, the electric resistivity of the vulcanizates containing channel black is exponentially reduced, and in the case of nozzle black it exponentially increases with a rise of temperature. Evidently a rise of temperature causes a certain degree of thickening of the carbon structures in the first case, and partial destruction of them in the second.

At temperatures above 100° C, another distinguishing property of channel black is revealed; the ρ value of vulcanizates containing channel black continues to fall exponentially, while the same property of a vulcanizate containing nozzle black, at a temperature above 100° C, increases faster than is represented

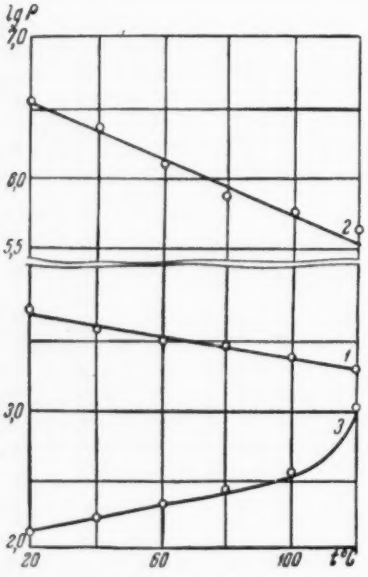


FIG. 1.—Specific resistivity of undeformed vulcanizates as a function of temperature. Vulcanized kok-saghyz rubber containing: 1. Channel black; 3. Nozzle black, and vulcanized butadiene-styrene rubber containing: 2. Chan-

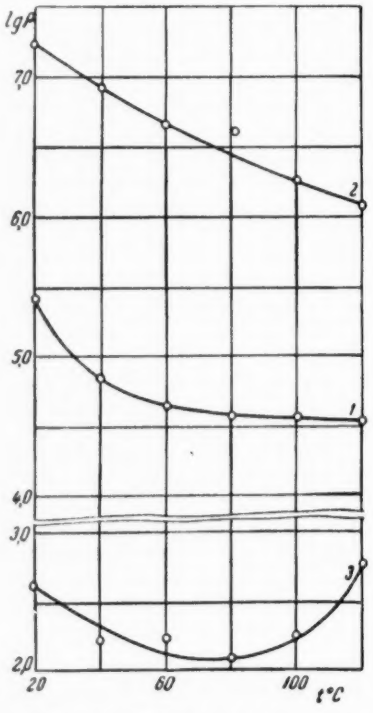


FIG. 2.—Change of specific resistivity of vulcanizates stretched 100 per cent as a function of temperature. Vulcanized kok-saghyz rubber containing: 1. Channel black. 3. Nozzle black, and vulcanized butadiene-styrene rubber containing: 2. Channel black.

by the exponential relation. Evidently in the latter case the destruction of the carbon structure at temperatures above 100° C becomes even more intensive.

If ρ is measured at various temperatures on specimens elongated up to 100 per cent, the nature of the relation is essentially changed (see Figure 2). The exponential law remains unchanged in this case. This is due to the superposition on the changes caused by a rise of temperature (first process) of changes caused by the orientation of elements of the carbon structure in the direction of stretching (second process). The second process, discussed in the previous work[1] causes the carbon structures in any part of the specimen to become more dense.

In the case of channel carbon black, both processes proceed in one direction, as a result of which the decrease of log ρ with temperature is more rapid than linear.

In the case of nozzle black, these processes proceed in opposite directions, and the change of log ρ with the temperature is represented by a curve having a

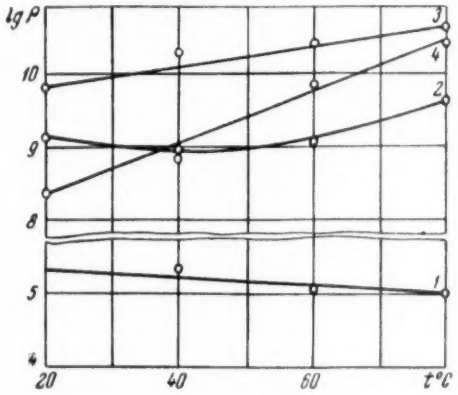


FIG. 3.—Temperature changes of specific resistivity of vulcanizates of sodium-butadiene rubber containing: 1. Channel black. 2. Furnace black. 3. Nozzle black. 4. Lamp black.

minimum; at low temperatures, the orientation process prevails and, at high temperatures, the destruction of the carbon structures.

Similar data were obtained for the series of vulcanized sodium-butadiene rubbers in the temperature interval of 20–80° C. These data are given in Table 2, and are depicted graphically in Figure 3. In these vulcanizates, too, the channel black structure is more resistant at elevated temperatures. Besides, the carbon-carbon bond of a given vulcanizate is stronger than the rubber-carbon bond. This follows from the fact that in the equation:

$$I = cV^n \tag{2}$$

relating the change of strength of a current I with the voltage V, the value of the coefficient n in the case of channel carbon black approaches unity with rise of temperature; this indicates an increase of the proportion of carbon-carbon bonds in the whole structural network. (The relation between the structural mixture and the increase of the coefficient n is discussed in a preceding paper[1]). In the case of nozzle black and lamp black with a rise of temperature, this coefficient departs further from unity; this indicates a decrease of the propor-

TABLE 2

Type of carbon black	Carbon black content in parts by weight per 100 parts rubber	20° C		40° C			60° C			80° C			
		ρ ohms per cm.	n_0	ρ ohms per cm.	n	$\frac{n_0}{n}$	ρ ohms per cm.	n	$\frac{n_0}{n}$	ρ ohms per cm.	n	$\frac{n_0}{n}$	α
Channel black	60	2.2×10^{5}	1.23	2.3×10^{5}	1.25	0.98	1.3×10^{5}	1.15	1.07	1.0×10^{5}	1.13	1.09	−0.015
Furnace black	70	1.4×10^{9}	2.08	8.7×10^{8}	2.00	1.04	1.3×10^{9}	2.28	0.91	3.7×10^{9}	2.41	0.86	−*
Nozzle black	75	6.3×10^{9}	3.50	2.1×10^{10}	3.84	0.91	2.5×10^{10}	—	—	4.4×10^{10}	4.1	0.85	+0.029
Lamp black	85	2.2×10^{8}	2.77	7.7×10^{8}	3.12	0.89	7.3×10^{9}	3.2	0.87	3.2×10^{10}	3.36	0.82	+0.089

* The coefficient α for the vulcanizate containing furnace black was not calculated, since in this case the relation of the temperature to log ρ was not linear (see Figure 3).

tion of carbon-carbon bonds in the structural network of the corresponding vulcanizates. Furnace black is, in this respect, in an intermediate position.

The strength of the carbon-carbon bond as a function of the temperature can be expressed by the same relation: n_0/n, that was applicable to the case of repeated deformation[1], as well as the coefficient α of Equation (1). For both

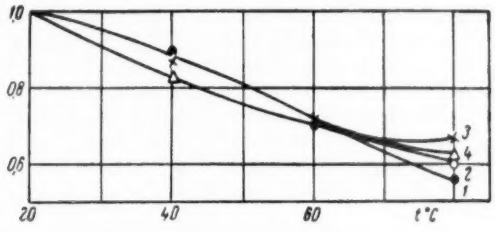


FIG. 4.—Relative change of tensile strength of vulcanizates of sodium-butadiene rubber containing: 1. Channel black. 2. Furnace black. 3. Lamp black. 4. Nozzle black.

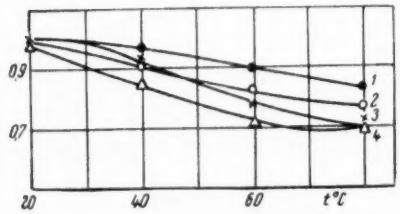


FIG. 5.—Relative change of elongation of vulcanizates of sodium-butadiene rubber containing: 1. Channel black. 2. Furnace black. 3. Lamp black. 4. Nozzle black.

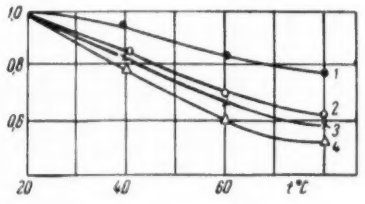


FIG. 6.—Relative change of tensile strength of vulcanizates of sodium-butadiene rubber containing: 1. Channel black. 2. Furnace black. 3. Lamp black. 4. Nozzle black.

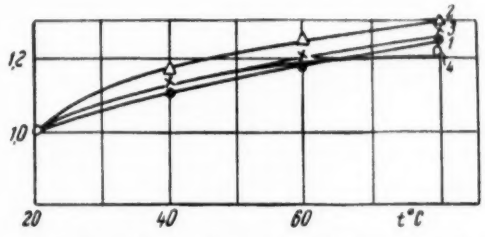


FIG. 7.—Relative change of elasticity (based on percentage of energy returned during elastic recovery) of vulcanizates of sodium-butadiene rubber containing: 1. Channel black. 2. Furnace black. 3. Lamp black. 4. Nozzle black.

these indexes, the carbon blacks studied fall in the same order as the order of their reinforcing effect in rubber.

As for the physical-mechanical properties of these vulcanizates, the relation of their coefficients of temperature stability to the temperature is expressed by uniform increasing or decreasing curves, parts of which are shown in Figures 4–7. A study of these curves leads to the conclusion that the high heat stability of the carbon black structures is most clearly indicated by the relatively high coefficient of temperature stability of the tensile strength of the rubbers con-

taining these carbon blacks (see Figure 6). The same, to a lesser degree, can be said of the coefficient of temperature stability as indicated by relative elongation (see Figure 5).

DESTRUCTION AND RESTORATION OF CARBON STRUCTURES AT VARIOUS TEMPERATURES

The experiment was performed thus: a specimen was held for 30 minutes at a given temperature, was stretched to 100 per cent elongation, and then was kept at constant temperature and elongation for 40–50 hours. The ρ value was measured before and after stretching after different time intervals from the time corresponding to the greatest value of ρ (ρ_m). This manner of investigation was necessitated by the fact that an elongation of 100 per cent, as shown in the preceding work[1], corresponds to the maximal value of the change of electric resistivity.

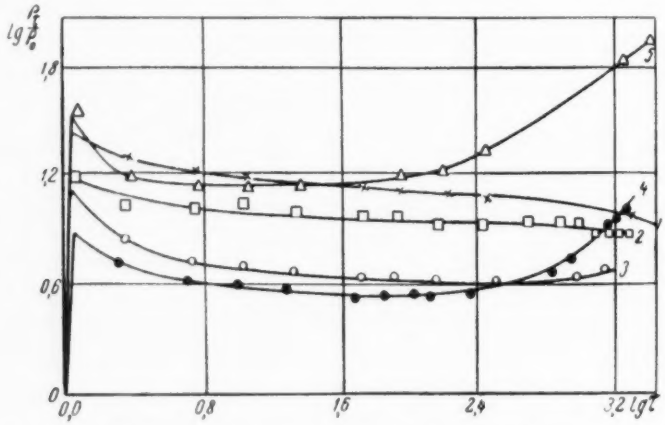


FIG. 8.—Kinetics of relative change of specific resistivity of a kok-saghyz rubber vulcanizate containing channel black at 100 per cent elongation at different temperatures: 1. Room temperature. 2. 40° C. 3. 60° C. 4. 80° C. 5. 100° C.

Figure 8 shows ρ_τ/ρ_0 as a function of time for vulcanizates of kok-saghyz rubber containing channel black; ρ_τ is the value of ρ in the given time interval, and ρ_0 is the initial value of ρ (before stretching) at the given temperature. Logarithmic coordinates were used in order to combine the curves of various temperatures in one figure. The curves show that, at all the temperatures studied, $\log \rho_\tau/\rho_0$ at the beginning decreases rapidly, and the initial rate of decrease increases with increase of temperature. Then the rate of decrease falls sharply, and approaches zero after 30–40 minutes (the higher the temperature, the sooner this takes place). Starting at a certain time interval at a temperature of 60° C or higher, $\log \rho_\tau/\rho_0$ again begins to increase.

A similar series of experiments was carried out on specimens of the same vulcanizate stretched to an elongation of 100 per cent and allowed to retract. The kinetic curves for this series are seen in Figure 9. Here too, the rate of decrease of $\log \rho_\tau/\rho_0$ increases with the temperature as the time curves approach zero. An increase of $\log \rho_\tau/\rho_0$ in these conditions is observed only at 100 per cent.

From the shape of the curves in Figures 8 and 9 and the order in which they are arranged the processes which take place for the specimens studied may be assumed to be the following. As was shown earlier, stress causes destruction of some of the contacts in the carbon structure. If the stretched specimen is kept at constant elongation and temperature, then the destroyed structure will be rebuilt, and the structural elements will be oriented in the direction of stress,

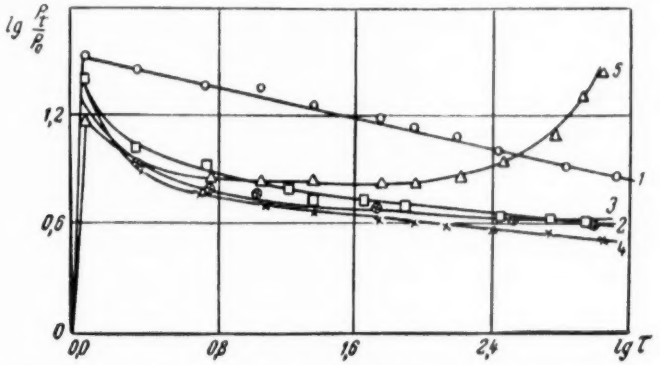


FIG. 9.—Kinetics of relative change of specific resistivity of vulcanized kok-saghyz rubber containing channel black at different temperatures. The specimens were stretched to elongation of 100 per cent and allowed to relax. 1. Room temperature. 2. 40° C. 3. 60° C. 4. 80° C. 5. 100° C.

causing a density of the structure and, consequently, a decrease of electric resistivity. However, at elevated temperatures, thermal decay is added to the process of restoration of the carbon black structures, as well as relaxation processes, which take place in the rubber itself. These processes, as is easily understood, can lead to a decrease of density of the carbon black conductors in any part of the specimen. The rates of the fundamental and the two accompanying processes, particularly the second of these, increase when the tempera-

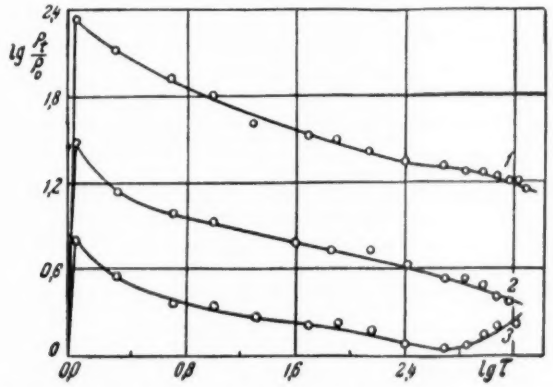


FIG. 10.—Kinetics of relative change of specific resistivity of vulcanized kok-saghyz rubber containing nozzle black at different temperatures; the specimens were stretched to 100 per cent and allowed to relax. 1. Room temperature. 2. 40° C. 3. 80° C.

ture is raised. The relation between the rates of these processes determines the shape of the kinetic curves (see Figure 8) at any temperature.

In specimens stretched and allowed to relax, the strain is nearly zero, and although there are no orientation processes here, the rate of the second process is considerably less than in stretched specimens. Therefore the increase of $\log \rho_\tau/\rho_0$ is observed at a higher temperature in relaxed than in stretched specimens (see Figure 9)

In vulcanizates containing nozzle black, an increase of temperature causes a more extensive destruction of the structure than in the case of channel carbon black. In addition to Figures 1 and 2 above, the curves in Figures 10 and 11 indicate this. From an examination of these curves, it is clear that stretching to a given elongation causes destruction of the structure proportionately less as the temperature is higher. Checking the course of the temperature curve of electrical resistance for a vulcanizate containing carbon black (see Figure 1),

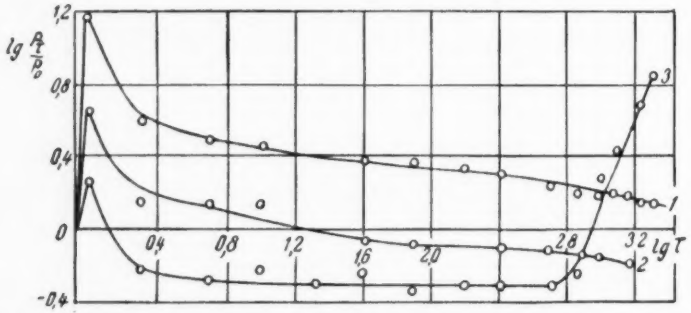


FIG. 11.—Kinetics of relative change of specific resistivity of vulcanized kok-saghyz rubber containing nozzle black at 100 per cent elongation at differentt emperatures. 1. Room temperature. 2. 40° C. 3. 80° C.

this fact can be explained only by partial destruction of the structure which takes place during heating of the specimen to the given temperature before deformation. In vulcanizates containing channel black, the degree of destruction of the structure during deformation depends less on the temperature; evidently in this case the basic factor causing destruction is the stretching, which is the same at all temperatures.

Table 3 gives the basic data for the degree of destruction:

$$\left(\left[1 - \frac{\log \rho_0}{\log \rho_m}\right] \cdot 100\%\right) \text{ and restoration } \left(\frac{\log \rho_0}{\log \rho_\tau} \cdot 100\%\right),$$

of carbon structures in vulcanizates of kok-saghyz rubber and butadiene-styrene rubber containing channel and nozzle carbon blacks.

Here ρ_0 is the specific resistivity at a given temperature (before deformation); ρ_m is the highest value of ρ during deformation and relaxation; ρ_τ is the value of ρ two hours after the measurement of ρ_m.

INTERPRETATION OF THE RESULTS

The state of the carbon black structure in any vulcanizate is determined by the relative strength of the rubber-carbon and carbon-carbon bonds for the given conditions of temperature, deformation, etc. The energy of heat move-

ment during heating in the rubber molecules and carbon particles tends to tear these apart, that is, to destroy both types of bonds. Naturally, in this process the weaker bonds are destroyed first, and the proportion of stronger bonds increases in the surviving structure.

From this it follows that in channel black structures, regardless of the type of rubber, heating (within the temperature limits studied) causes an increase of the proportion of carbon-carbon bonds, which are stronger in this system. In structures of furnace, nozzle, and lamp blacks, on the contrary, heating decreases the proportion of carbon-carbon bonds, which are the weaker ones in these systems. Thus, a study of the behavior of various carbon structures during rise of temperature leads to the same conclusions concerning the relative strength of the bonds in carbon structures that were reached in the preceding work[1] on the influence of repeated deformations.

The bonds destroyed during deformation are partially restored in the relaxation process. The rate of restoration of all carbon structures depends on the conditions of deformation and relaxation, and is determined by the relations of the processes. It follows from the above that the basic processes which take place during the stretching and relaxation of heated specimens are the following:

1. The destruction of a part of the rubber-carbon and carbon-carbon bonds by the formation of critical stresses which cause a decrease of density of the carbon structures in the specimen.
2. Orientation of the remaining elements of the carbon structure in the direction of deformation, together with the formation of temporary contacts, causing an increase of density of the carbon structures. When the deformed specimen retracts, the temporary contacts are destroyed; consequently the real degree of destruction can be judged only in the shortened specimens.
3. The destruction of a part of the rubber-carbon and carbon-carbon bonds, caused by heat movement of the rubber molecules and carbon particles, which leads to a decrease of density of the carbon structures in the specimen.
4. The formation of new bonds caused by collisions during heat movement, leading to an increase of density of the carbon structures in the specimen.

In deformed, but unretracted specimens, the presence of stresses facilitates processes (1) and (2), and reduces process (4) to a minimum. In the same specimens, an increase of temperature activates processes (1), (3), and (4).

In specimens which have relaxed after deformation in which the stress is nearly zero, an increase of temperature activates the latter two processes, principally process (4), that is, the weakest bonds are already destroyed during stretching.

A combination of all four processes causes a change in the nature of the carbon structures. The data in Table 3 show that the nature of these changes is determined principally by the type of carbon black present. Thus, for example, the degree of destruction of channel carbon structures during deformation in both rubbers studied changes relatively little when the temperature is increased from 20° to 80° C. Clearly, then, in the case of channel carbon black the role of process (3) is less than that of processes (1) and (2). On the other hand, in the case of nozzle black, the destruction of the structure during deformation decreases considerably when the temperature is increased; evidently the role of process (3) in this case is quite important. The same can be said of the degree of restoration of the carbon structures, for which process (4) is of much more importance in the case of nozzle black then in that of channel black. The nozzle black structure, destroyed largely through the action of mechanical

TABLE 3

DESTRUCTION AND RESTORATION OF CARBON BLACK STRUCTURES AT DIFFERENT TEMPERATURES

Type of rubber and carbon black	ρ ohm per cm. at 20° C	Conditions at which specimen was kept: Temperature in ° C	Conditions at which specimen was kept: Elongation in %	ρ_0 ohms per cm.	ρ_m ohms per cm.	ohms per cm.	$\left[1-\frac{\log \rho_0}{\log \rho_m}\right]\cdot 100\%$	$\frac{\log \rho_0}{\log \rho_T}\cdot 100\%$
Kok-saghyz and channel black	1.8×10^{4}	20	100	1.8×10^{4}	4.7×10^{5}	2.4×10^{5}	25.0	79.2
	1.5×10^{4}	80	100	4.7×10^{3}	4.3×10^{4}	1.6×10^{4}	20.7	87.3
	1.4×10^{4}	20	20*	1.4×10^{4}	4.5×10^{5}	1.7×10^{5}	26.8	79.2
	1.3×10^{4}	80	20	3.6×10^{3}	8.8×10^{4}	1.4×10^{4}	27.8	86.1
Butadiene-styrene rubber and channel black	2.7×10^{6}	100	50	1.3×10^{5}	2.4×10^{6}	6.9×10^{5}	19.8	87.8
	5.6×10^{6}	100	100	2.6×10^{5}	3.4×10^{6}	9.7×10^{5}	17.0	90.5
Kok-saghyz and nozzle black	1.7×10^{2}	20	100	1.7×10^{2}	2.5×10^{3}	3.7×10^{2}	34.3	86.8
	87.0	80	100	1.6×10^{2}	3.7×10^{2}	1.1×10^{2}	24.2	108.0
	93.0	20	20*	93.0	2.0×10^{3}	2.3×10^{2}	40.3	83.5
	1.8×10^{2}	80	20	4.7×10^{2}	1.1×10^{3}	2.3×10^{2}	22.2	113.0

* The specimens were stretched up to 100 per cent elongation and allowed to relax to 20 per cent elongation.

and temperature factors after the stress is removed, is restored to a larger degree than the channel carbon structure. This is evident from a comparison of the indexes in the last two columns of Table 3. For example, at 20° C, destruction of the structure in deformed and relaxed specimens is 26.8 per cent for rubber containing channel black and 40.3 per cent for rubber containing nozzle black; that is, under equal conditions the nozzle black structure is destroyed 1.5 times as much. Two hours after removal of stress, the index of structure-rebuilding is 79.4 per cent for rubber containing channel black and 83 per cent for rubber containing nozzle black. At 80° C, the index of structure rebuilding is 86 and 113 per cent, respectively.

The results obtained make possible a number of conclusions about the nature of the forces acting between rubber and carbon blacks and the mechanism of reinforcing rubber. However, the discussion of these questions will be left for the next article.

CONCLUSIONS

1. Raising the temperature of vulcanizates containing carbon black causes changes in the carbon structures, which can be estimated by the value of specific electric resistivity ρ and the index n in the equation: $I = cV^n$, relating the strength of the current I with the voltage V.

2. These changes are nearly independent of the type of rubber and are governed chiefly by the type of carbon black.

3. The change of electric resistivity of vulcanizates with temperature follows an exponential law, and can be expressed by the equation: $\rho_t = \rho_0 e^{\alpha t}$.

4. The sign of the coefficient α is negative for vulcanizates containing channel carbon black, and positive for those containing nozzle black or lamp black.

5. Heating of vulcanizates (up to 100°) for 30 minutes causes destruction of the nozzle black and lamp black particles, but causes little apparent destruction of channel black structures.

6. Prolonged heating (10 hours or more) at temperatures above 60° C causes destruction of the particles of all the carbon blacks studied. This destruction is more extensive in the case of nozzle and lamp blacks than in the case of channel black.

7. During heat treatment of mixtures containing channel black, it is chiefly the carbon-rubber bonds that are destroyed (the index n decreases); whereas in mixtures containing nozzle, furnace and lamp blacks, it is chiefly the carbon-carbon bonds that are destroyed (the index n increases).

8. The higher the temperature during deformation and relaxation, the greater is the degree of restoration of the carbon structures which are destroyed during deformation.

9. The degree of restoration of the carbon structures under identical conditions of deformation and relaxation of vulcanizates containing nozzle black is greater than that of corresponding vulcanizates containing channel black.

REFERENCES

[1] Dogadkin, Pechkovskaya, and Mil'man, *Kolloid. Zhur.* **4**, 260 (1952).
[2] Bulgin, *Trans. Inst. Rubber Ind.* **21**, 188 (1945); Wack, Anthony, and Guth, *J. Applied Physics* **18**, 456 (1947).

THE EFFECT OF COMONOMER ON THE MICROSTRUCTURE OF BUTADIENE COPOLYMERS *

FREDERICK C. FOSTER AND JOHN L. BINDER

CHEMICAL AND PHYSICAL RESEARCH LABORATORIES, THE FIRESTONE TIRE & RUBBER CO., AKRON, OHIO

It is well-known that butadiene polymerizes by 1,2-addition to produce side vinyl (—CH=CH_2) groups and, by 1,4-addition, to produce double bonds in the polymer chain with *cis*- and *trans*-configurations. With butadiene-vinyl copolymers the diene portion of the copolymer chain may also have any or all of the three microstructures mentioned above. It is known[1] that, in general, increasing the temperature of polymerization, for both types of polymers, increases the amount of *cis*-1,4-addition and decreases the amount of *trans*-1,4-addition. It is also known that a variation in the mechanism of polymerization causes a change in the microstructure of butadiene polymers; thus, 1,2-addition predominates in sodium-catalyzed butadiene polymers.

Little or nothing is known about the effect of the kind or concentration of the vinyl comonomer on the microstructure of the diene polymer. Thus early workers[2] by ozonolysis concluded that copolymers of butadiene with methyl methacrylate and methacrylonitrile probably contained more 1,4-addition than polybutadiene. Early infrared work[3] indicated that butadiene-styrene or butadiene-acrylonitrile copolymers had smaller amounts of 1,2-addition than polybutadiene. However, Kolthoff, Lee and Mairs[4], using the perbenzoic acid method, reported that the amount of 1,2-addition did not vary with kind or concentration of the comonomer in butadiene copolymers. Hart and Meyer[5], on the basis of infrared measurements, concluded that the amount of styrene had no effect on the amounts of 1,2- and 1,4-addition in the butadiene portion of butadiene-styrene copolymers. However, their data show a slight increase of *trans*-1,4-addition with a corresponding decrease of *cis*-1,4-addition as the styrene concentration was increased from 0 to 23 per cent.

With many of the butadiene copolymers reported above, the range of concentration of the comonomer was small and the experimental uncertainties too large to show small trends. Therefore the effect of kind and concentration of the comonomer in butadiene-vinyl copolymers was investigated, in the present work, using large concentration ranges. Because of the dependence of microstructure on temperature and polymerization mechanism, all of the polymers reported here were prepared at the same temperature using free radical catalysis.

EXPERIMENTAL

All vinyl monomers were purified by distillation before use. Monomers were tested for the absence of polymer before use. Physical constants found for the monomers were: acrylonitrile, n_D^{20} 1.3916; methacrylonitrile, n_D^{20} 1.4005;

* Reprinted from the *Journal of the American Chemical Society*, Vol. 75, No. 12, pages 2910–2913, June 20, 1953.

α-methylstyrene, n_D^{20} 1.5386, methylvinyl ketone, n_D^{20} 1.4117; 2-vinylpyridine, n_D^{20} 1.5482, and styrene, n_D^{20} 1.5468.

Butadiene, supplied by Koppers Company and meeting Rubber Reserve standards of purity, was merely condensed before use.

All copolymerizations were conducted at 50°, using the following recipe:

Water	180
Monomers	100
S F Flakes	5
Potassium persulfate	0.3
Dodecanethiol	0.75

Conversions were varied from low to complete conversion.

Copolymers were coagulated with methanol and washed several times with water and with methanol. Final purification was accomplished by extracting the copolymers under gentle reflux with ethanol-toluene azeotrope (70-30 by volume). Three changes of solvent were used, each extraction lasting an hour. The copolymers were then extracted three times with acetone and dried under vacuum. It was necessary to substitute methanol for acetone in the final extractions of the acrylonitrile copolymers, methacrylonitrile copolymers and the high styrene copolymers in order to avoid dissolving some of the copolymer. In the case of methyl vinylketone copolymers, it was necessary to extract only with methanol.

The composition of butadiene-styrene copolymers was determined by refractive index. The method used was essentially that developed by the Bureau of Standards[6]. Copolymers, high in styrene, did not wet the prisms and Thoulet's solution was used to establish contact with the prism in these cases. The relation between refractive index and styrene content, which is not linear over the complete range of compositions, was determined from copolymers of known composition. This relationship agrees with previously determined work[7].

Copolymer compositions for the systems butadiene-acrylonitrile, butadiene-methacrylonitrile and butadiene-vinyl pyridine were determined by the Friedrich micro-Kjeldahl method for nitrogen analysis. Carbon determination, by combustion, was used in the analysis of butadiene-methylvinyl ketone copolymers. The composition of one of the butadiene-α-methylstyrene copolymers was calculated from initial charge, having been taken to complete conversions.

The determinations of the amounts of *cis*-1,4, *trans*-1,4- and 1,2-additions, as well as styrene, were made by a spectroscopic method developed in these laboratories, which is partially described elsewhere[8]. Essentially it consists of measuring the intensities of the bands at 10.34, 10.98, 14.7 and 14.29 μ for *trans*-1,4-, 1,2-(terminal vinyl groups), *cis*-1,4- and styrene components, respectively, and assuming that Beer's law holds for the components and the mixture as exemplified by the equations:

$$D_i = e_{ij}c_jl + e_{ik}c_kl + e_{im}c_ml + e_{in}c_nl$$

where D_i is the optical density at wave length i, e_{ij}, e_{ik}, etc., are the extinction coefficients at wave length i of components j, k, m, etc., the c's are concentrations in moles per l. or g. per l., and l is the length of light path in cm.

In the styrene determinations, it was essential to correct for the deviations from Beer's law, as exhibited by the optical density *vs.* concentration curve for polystyrene, and to purify the polymers by the Bureau of Standards extraction procedure in order to obtain values which agreed with those found by refractive index measurements. The trustworthiness of the results is indicated by the "Total found" (Column 6 of Table I), which is the amount of polymer found in the solution by the infrared analyses, compared with that determined from the total solids of the solution. This value should be equal to or less than 100 per cent depending upon how many of the diene double bonds are saturated. Analyses of polybutadienes by this method have given values for the total unsaturation which agree with those found chemically within the experimental error of the latter method.

The copolymers studied here were analyzed by this method, with the following variations in the case of those comonomers for which it was impossible

TABLE I

COMPOSITIONS OF BUTADIENE–STYRENE COPOLYMERS BY INFRARED METHOD

cis-1,4 BD = 100 (%)	*trans*-1,4 BD = 100 (%)	1,2 BD = 100 (%)	Styrene by infrared (%)	Styrene by refractive index (%)	Total styrene and diene by infrared (%)	
13.4	77.6	9.2	87.0	86.3	99.4	
12.3	77.6	10.1	86.8	85.5	102.8	
14.0	75.2	10.9	80.5	78.5	103.2	
14.1	73.9	12.0	72.9	71.7	97.6	
13.6	73.0	13.4	59.9	60.1	95.9	
16.2	70.0	13.7	64.1	59.0	101.7	
12.0	70.0	18.2	55.8	57.1	103.9	
17.5	67.6	14.9	50.3	49.0	101.5	
16.0	68.5	15.5	41.9	40.1	99.3	
17.4	66.9	15.6	30.8	27.7	103.5	
16.7	65.8	17.6	23.9	22.7	100.1	
15.3	65.7	19.1	21.1	21.7	104.0	
19.6	63.4	17.0	0		96.0	Duplicate analyses
19.0	63.7	17.4	0		94.8	

to make calibration curves. The optical densities were measured at the band maxima even though, with some polymers, these may have shifted somewhat from 10.34, 10.98, or 14.70 μ. The α-methylstyrene was considered to absorb the same as styrene at 10.34, 10.98, 14.7 and 14.29 μ and the polymers analyzed as butadiene-styrene copolymers. No correction for the deviation from Beer's law was made for the α-methylstyrene however. The spectra of homopolymers of the other vinyl comonomers showed that there are no other strong bands in the vicinities of the bands at 10.34, 10.98 and 14.7 μ due to polybutadiene, and these copolymers were then analyzed simply as polybutadienes. This means that the contributions of the comonomer absorption at these wave lengths were neglected, which should result in the amount of polybutadiene found in the copolymer by the analysis being larger than that found chemically. Actually the two results agree surprisingly well for most of the copolymers studied here, which means that the absorptions of the comonomers at the wave lengths used for the polybutadiene analyses must be small. Consequently, it is thought that the results obtained are reliable to about 2 per cent.

RESULTS

Table I gives the analyses of butadiene-styrene copolymers by the spectroscopic method and also the amount of styrene found by refractive index. In this table the values under the headings BD = 100 refer to the composition of the butadiene portion of the polymer. The average deviation of the styrene determined spectroscopically and by refractive index is 1.7 per cent. Most of the high totals shown in the table are due to the larger amounts of styrene found spectroscopically. The two exceptions are the two polymers with the highest totals; these were low conversion polymers, and the presence of a small amount of styrene monomer might explain both the high totals and the anomalous microstructure values. The actual percentages of the three diene structures may be computed from Table I by subtracting the value in column 4 from the

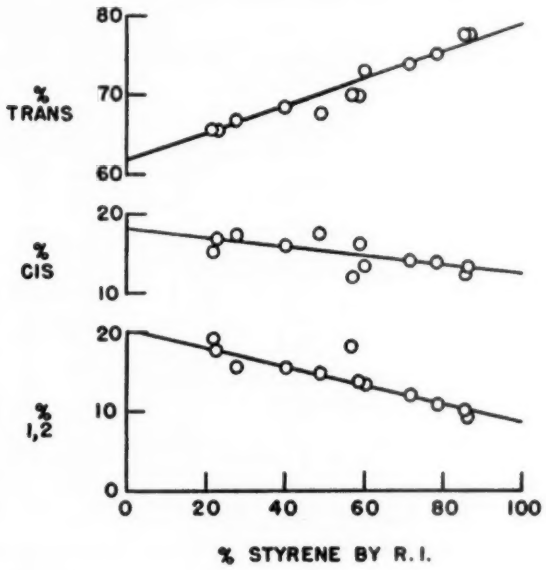


FIG. 1.—Microstructure *vs.* styrene content of butadiene-styrene copolymers.

value in column 6 and multiplying the quantity by the value in each of the first three columns.

The data show that, as the amount of styrene in the polymer increases, the proportion of *trans*-1,4-addition increases and the proportions of *cis*-1,4- and 1,2-additions decrease. Enough polymerizations were run to various conversions to establish that the conversion has no effect on the microstructure of the polymers.

Figure 1 shows graphically the relationships between the amount of styrene (by refractive index) in the copolymer and the amounts of *cis*-1,4-, *trans*-1,4- and 1,2-additions in the butadiene portion of the polymer. These relationships are linear within experimental error.

Table II gives experimental results of microstructures of several other butadiene copolymer systems. All of the comonomers investigated apparently are

similar to styrene in their effect on microstructure and differ only in the magnitude of this effect. For these copolymers the ranges of concentration and the analytical accuracy are not great enough to show unambiguously the effect of different concentrations of comonomer. The effect of kind of comonomer is clearly shown, however, by comparing these copolymers either with polybutadiene or butadiene-styrene copolymers of similar butadiene content given in Table II.

DISCUSSION

Alfrey[9] has emphasized that the microstructure of a given butadiene unit is not determined at the time when the butadiene molecule is attacked by the growing chain, but rather at the time of the subsequent propagation step, when the butadiene radical attacks the next monomer. In copolymerization reac-

Table II

Microstructure of Butadiene Portion of Diene–Vinyl Copolymers

Vinyl comonomer	*cis*-1,4 BD = 100 (%)	*trans*-1,4 BD = 100 (%)	1,2 BD = 100 (%)	Butadiene by infrared (%)	Butadiene chemically (%)
α-Methylstyrene	20.1	73.0	6.9	27.6	
	14.2	77.0	8.7	37.6	
	17.8	64.8	17.4	53.7	
	17.6	69.1	13.3	55.8	
	18.8	64.4	16.8	77.7	80.1[a]
Vinylpyridine	18.0	70.4	11.7	24.7	24.6[b]
	14.2	71.6	14.2	50.1	46.5[b]
	16.7	66.5	16.8	61.9	61.2[b]
	18.8	64.9	16.4	68.0	74.6[b]
Methylvinyl ketone	13.8	72.7	13.5	62.4	59.6[c]
	16.1	69.7	14.2	70.5	68.9[c]
	17.5	76.4	15.0	75.1	71.6[c]
Acrylonitrile	14.6	76.2	9.3	72.0	75.4[b]
	12.4	77.1	10.5	76.9	76.1[b]
	16.7	72.3	11.0	72.8	78.0[b]
Methacrylonitrile	15.9	75.5	8.6	56.8	67.6[b]
	14.9	75.1	10.0	62.8	71.6[b]
	14.1	71.3	14.5	73.1	78.2[b]

[a] Based on initial charge and complete conversion.
[b] Nitrogen analyses.
[c] Carbon analyses.

tions of butadiene, this subsequent propagation step may involve reaction with either butadiene monomer or the comonomer. It does not seem surprising that the structure of the monomer in this latter step would, in general, affect the proportions of the three diene structures in the resultant polymer. Therefore, in general, the percentages of *cis*-1,4-, *trans*-1,4- and 1,2-structures would be expected to be different from those for polybutadiene and, in fact, vary as the type of comonomer is varied. It would also follow that the change in the microstructure of diene copolymers would increase as the comonomer content of the copolymer is increased.

Considering that only the two propagation reactions involving diene free radicals affect microstructure, while all four propagation reactions affect copolymer composition, kinetic calculations show that structure should depend linearly on the quantity $1/(1 + r_1[D]/[V])$, where r_1 is the reactivity ratio for the diene and [D] and [V] refer to the mole fractions of diene and vinyl

monomer, whereas the copolymer composition depends linearly on the quantity $(1 + r_2[V]/[D])/(2 + r_1[D]/[V] + r_2[V]/[D])$. These two quantities become identical only when $r_1 = 1/r_2$. Figure 2 shows the expected relationship of copolymer composition and microstructure for three different types of copolymers. These curves were calculated from the above algebraic expressions which relate to the structure and composition of an initial copolymer (*i.e.*, zero conversion), since they were derived from differential equations. Considering an example in which the polydiene contains 20 per cent of the 1,2-structure and the percentage of 1,2-structure approaches zero as a limit at 100 per cent vinyl content, a 50–50 copolymer, on a mole basis, of type A should contain about 2 per cent 1,2-addition, a similar type B polymer should contain 10 per cent 1,2-addition, and a corresponding type C polymer should contain about 18 per cent 1,2-addition, all based on the diene portion of the copolymer.

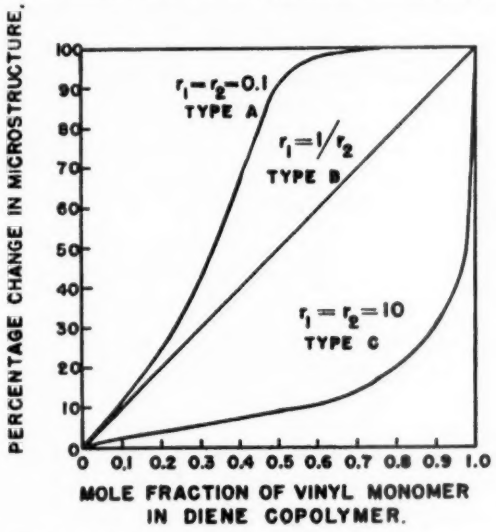


FIG. 2.—Variation of microstructure with composition of initial copolymers.

Type C copolymers, in which both reactivity ratios are greater than 1, do not exist in practice. Type A copolymers, in which both reactivity ratios are less than 1, are quite common. These copolymers are examples of the alternating effect which is so prevalent in free radical copolymerizations. The system butadiene-acrylonitrile is of this type; reactivity ratios are 0.35 and 0.05[10], respectively. This undoubtedly accounts for the large change in microstructure when approximately 25 per cent acrylonitrile enters a butadiene polymer (see Table II). The change in percentage of 1,2 is larger than could possibly be accounted for on an additive basis, but consistent with the theoretical considerations outlined above.

The reactivity ratios for butadiene-styrene are 1.4 and 0.5, respectively[11]. This system closely approximates Type B in which one reactivity ratio is the reciprocal of the other. Thus, the microstructure theoretically should vary almost linearly with styrene content; experimental data in Figure 1 are consistent with this.

The data indicate that acrylonitrile monomer causes the greatest change in polybutadiene microstructure, followed by methacrylonitrile. The other four comonomers, styrene, α-methylstyrene, vinylpyridine and methylvinyl ketone, exert approximately the same effect on microstructure, within the precision of the data. Although this greater change in microstructure associated with acrylonitrile and methacrylonitrile copolymers may be partially explained by the greater alternating tendency in these copolymer systems (Type A in Figure 2), some of this greater change must be attributed to a greater effect of these two monomers on the diene microstructure. For example, as styrene content approaches 100 per cent the percentage of 1,2-addition approaches about 8 per cent as a limit (see Figure 1); whereas the 1,2-addition is approaching 0 per cent as a limit as the acrylonitrile or methacrylonitrile content approaches 100 per cent. In fact, the change of per cent 1,2-addition with comonomer content in the case of acrylonitrile copolymers is slightly greater than that theoretically allowable assuming 0 per cent 1,2-addition as the limiting value and indicates some error in either composition or microstructure in this case.

It may be significant that there is an apparent correlation between the magnitude of the effect of a comonomer on butadiene microstructure and the partial charge at the double bond of the comonomer. Thus, of all comonomers studied, acrylonitrile has the most positive e value[12], with methacrylonitrile the next most positive e value. Further work would be desirable to establish the relationship between comonomer structure and effect on microstructure on a more quantitative basis.

An attempt was made to correlate the effect of comonomers on diene microstructure with deviations from the Q and e theory for these same diene copolymer systems. Wall[13] was the first to point out that the Q and e theory often markedly fails when diene monomers are considered. He suggested addition of a parameter e^* for the diene radical different from the e for the corresponding diene monomer. Although the experimental data on chloroprene copolymerizations do illustrate the defection of the Q and e theory in the case of this diene, the experimental data on butadiene copolymerizations do not support a failure of the Q and e theory in this case, caused either by the difference in polarity between monomer and radical for dienes as proposed by Wall or by the differences in diene microstructure as comonomer is varied that is disclosed in the present work.

SUMMARY

The microstructure of butadiene-styrene copolymers having a wide range of styrene contents has been determined by infrared absorption. The results demonstrate that the percentage of *trans*-1,4-addition increases, the 1,2-addition decreases, and the *cis*-1,4-addition decreases as the styrene content is increased. Similar measurements of five other butadiene copolymer systems indicate that all these vinyl monomers, acrylonitrile, methacrylonitrile, methylvinyl ketone, vinylpyridine, and α-methylstyrene, change the microstructure in the same direction as styrene, differing only in the magnitude of their effect. A theoretical explanation, consistent with the experimental results obtained, is given for the change in microstructure with comonomer content.

ACKNOWLEDGMENT

The authors are indebted to Maxine Bender, who performed all of the nitrogen and carbon analyses. The authors wish also to express their appreci-

ation to F. W. Stavely for his continued interest in this work and to the Firestone Tire and Rubber Company for permission to publish these results.

REFERENCES

[1] Meyer, *Ind. Eng. Chem.* **41**, 1570 (1949).
[2] Hill, Lewis, and Simonson, *Trans. Faraday Soc.* **35**, 1067, 1073 (1939); Alekseeva, *J. Gen. Chem. USSR* **11**, 353 (1941); RUBBER CHEM. & TECHNOL. **15**, 698 (1942).
[3] White, J. U., and Flory, P. J., private communication to Office of Rubber Reserve, Reconstruction Finance Corporation, February 20, 1943.
[4] Kolthoff, Less, and Mairs, *J. Polymer Sci.* **2**, 220 (1947).
[5] Hart and Meyer, *J. Am. Chem. Soc.* **71**, 1980 (1949).
[6] Arnold, Madorsky, and Wood, *Anal. Chem.* **23**, 1656 (1951).
[7] D'Ianni, Hess, and Mast, *Ind. Eng. Chem.* **43**, 319 (1951); McPherson, A. T., private communication to Office of Rubber Reserve, Reconstruction Finance Corporation, January 3, 1950.
[8] Binder, J. L., private communication to Office of Rubber Reserve, Reconstruction Finance Corporation, June 25, 1951.
[9] For a derivation of this equation, see Bigeleisen, *Science* **110**, 14 (1949), and Bigeleisen and Friedman, *J. Chem. Physics* **17**, 998 (1949).
[10] Mayo and Walling, *Chem. Revs.* **46**, 218 (1950).
[11] Meehan, *J. Polymer Sci.* **1**, 318 (1946). Other values (*cf.* Mayo and Walling, *Chem. Revs.* **46**, 212 (1950)) reported for this system were calculated from an assumption of a linear relationship between refractive index and styrene content. It has been confirmed by several workers (*cf.* D'Ianni, Hess, and Mast, *Ind. Eng. Chem.* **43**, 319 (1951), McPherson, A. T., private communication to Office of Rubber Reserve, Reconstruction Finance Corporation, January 31, 1950) that this assumption is incorrect.
[12] Price, *J. Polymer Sci.* **3**, 772 (1948); Alfrey and Price, *J. Polymer Sci.* **2**, 101 (1947).
[13] Wall, *J. Polymer Sci.* **2**, 542 (1947).

SELF-INHIBITION IN THE OXIDATION OF BUTADIENE-ACRYLONITRILE RUBBERS *

A. S. Kuzminskiĭ and E. B. Popova

Scientific Research Institute of the Rubber Industry, Moscow, USSR

Because of their valuable technical properties, copolymers of butadiene and acrylonitrile rubbers have found wide use in the rubber industry in the production of oil-resistant and heat-resistant products.

Investigations have established that, during the copolymerization of butadiene with acrylonitrile, the latter enters principally at the 1,4-position of the main chain. This is observed most clearly with relatively large concentrations of acrylonitrile. Our own work[1] showed that the double bonds in the main chains of the rubber molecules are the most active points in the chain. It indi-

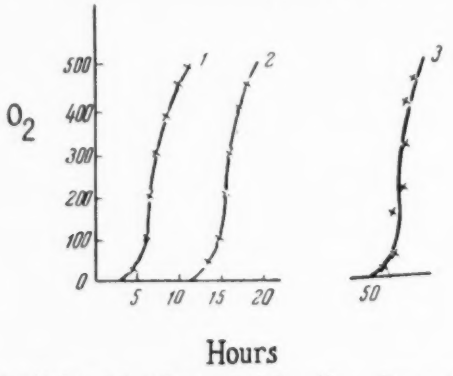


Fig. 1.—Kinetics of oxidation of butadiene-acrylonitrile rubbers. Temperature 120° C. Initial concentration of phenyl-β-naphthylamine 12.5 millimoles per mole.
1. CKH-18. 2. CKH-26. 3. CKH-40.
O_2 is amount of oxygen absorbed in millimoles per mole.

cated also that butadiene-acrylonitrile rubbers should oxidize at a fast rate. However, in reality they show great chemical stability.

The present study is devoted to an explanation of the nature of oxidation of butadiene-acrylonitrile rubbers. Both the free and inhibited oxidation of copolymers containing, respectively, 20, 29.6 and 35 per cent of acrylonitrile (CKH-18, CKH-26, and CKH-40) was studied.

Before oxidation, the rubbers were purified by extraction and double precipitation from benzene solutions. The rubber films were prepared and oxidized with molecular oxygen according to methods described previously[2].

Figure 1 shows the kinetic curves of oxidation of butadiene-acrylonitrile rubbers. As is seen, the induction periods of oxidation of butadiene-acrylonitrile rubbers increase with an increase of the acrylonitrile content in the copolymers. During the oxidation of butadiene-acrylonitrile rubbers, 10–15 per cent of byproducts soluble in ethyl alcohol are formed.

* Translated for Rubber Chemistry and Technology by Alan Davis from *Doklady Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik*, Vol. 58, No. 5, pages 1077–9 (1952).

If the byproducts of oxidation, extracted with alcohol, are added to polybutadiene rubber and the latter is oxidized, then, as Figure 2 shows, the kinetic curve of oxidation will show a long induction period. It should be pointed out that the addition of unoxidized butadiene-acrylonitrile rubber to polybutadiene rubber has no noticeable effect on the kinetics of oxidation of the latter.

Thus, the byproducts of the oxidation of butadiene-acrylonitrile rubbers have inhibiting properties. It follows that the inhibitor is formed as a result

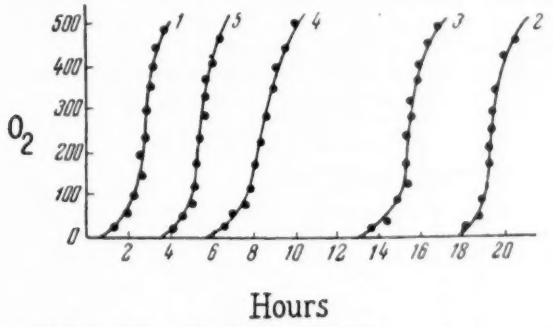


FIG. 2.—Influence of byproducts of oxidation of CKH-40 on kinetics of oxidation of sodium-butadiene rubber.

1. Oxidation of sodium-butadiene rubber
2. Oxidation of sodium-butadiene rubber with inhibitor of CKH-40 (CKH-40 was oxidized 0.5 hour)
3. Oxidation of sodium-butadiene rubber with inhibitor of CKH-40 (oxidized 1 hour)
4. Oxidation of sodium-butadiene rubber with inhibitor of CKH-40 (oxidized 2 hours)
5. Oxidation of sodium-butadiene rubber with inhibitor CKH-40 (oxidized 6 hours)

O_2 is amount of bound oxygen in millimoles per mole

of the oxidation of segments of the molecular chains which contain nitrile groups. It was shown that the byproducts of oxidation of butadiene-acrylonitrile rubbers extracted with alcohol contain nitrogen.

Only the byproducts of oxidation of butadiene-acrylonitrile rubbers possess inhibiting properties. None of the other synthetic or natural rubbers known to us forms oxidation byproducts capable of inhibiting the oxidation process.

The action of an inhibitor is greatly increased by the addition of phenyl-

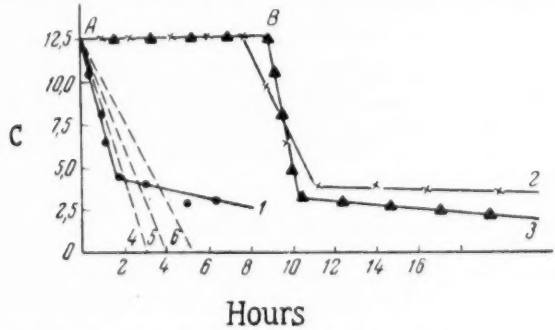


FIG. 3.—Kinetics of consumption of phenyl-β-naphthylamine in the process of oxidation of various rubbers. Temperature 120° C. Initial concentration of phenyl-β-naphthylamine 12.5 millimoles.

1. CKH-18. 2. CKH-26. 3. CKH-40. 4. Natural rubber (hydrocarbon). 5. Butadiene-styrene rubber. 6. Sodium-butadiene rubber.

C is concentration of phenyl-β-naphthylamine in millimoles per mole

β-naphthylamine to the rubber. As is seen in Figure 3, the nature of the kinetic curves of butadiene-acrylonitrile rubbers differs radically from that of those indicating the consumption of this inhibitor in natural, butadiene-styrene, and sodium-butadiene rubbers.

As has been established, the protective action of inhibitors is related to their slow rate of consumption; in the beginning of oxidation of butadiene-acrylonitrile rubbers (segment AB of curve 3), no consumption of phenyl-β-naphthylamine is observed. However, the solubility of the rubbers (Figure 4) and, consequently, their structure during this period, remains almost unchanged. Therefore, the rubbers are effectively protected.

The linear consumption of phenyl-β-naphthylamine and the abrupt decrease of solubility of the rubbers are observed simultaneously only after the initial

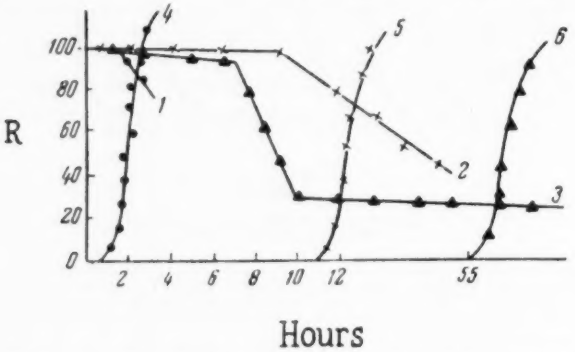


FIG. 4.—Change of solubility of butadiene-nitrile rubbers during oxidation at 120° C. Initial concentration of phenyl-β-naphthylamine was 12.5 millimoles per mole.

1. Solubility of CKH-18
2. Solubility of CKH-26
3. Solubility of CKH-40
4. Oxidation of CKH-18
5. Oxidation of CKH-26
6. Oxidation of CKH-40

R is quantity of dissolved rubber in percentage.

period of the reaction referred to above. A probable explanation of this phenomenon is that inhibitors form with phenyl-β-naphthylamine a new effective inhibitor.

The radical of this inhibitor, formed after the reaction with the rubber peroxides, evidently is isomerized and loses its inhibiting power. This byproduct gives the same light reactions as phenyl-β-naphthylamine. The tendency of the products of oxidation of butadiene-acrylonitrile rubbers to isomerize was shown by several convincing examples.

The isomerized inhibitor is not able to check the development of the autocatalytic process, and the rate of oxidation increases considerably in its presence. Thus the cause of the increased chemical stability of butadiene-acrylonitrile rubbers is due to the fact that, in the initial stages of their oxidation, byproducts are formed which effectively inhibit any further development of the process.

REFERENCES

[1] Kuzminskil and Lezhnev, *Doklady Akad. Nauk USSR* **40**, 6, 1021 (1950).
[2] Kuzminskil, Shanin, Degteva, and Lapteva, *Kolloid. Zhur.* **9**, 5, 377 (1947); Kuzminskil and Lezhnev, *Zhur. Fiz. Khim.* **24**, 5, 539 (1950).

ACRYLIC ELASTOMERS

PREPARATION AND PROPERTIES OF VULCANIZABLE ACRYLIC ESTER-ACRYLONITRILE COPOLYMERS *

E. M. Filachione, T. J. Fitzpatrick, C. E. Rehberg, C. F. Woodward, W. E. Palm, and J. E. Hansen

Eastern Regional Research Laboratory, Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture, Philadelphia, Pennsylvania

Earlier investigations at this Laboratory[1] resulted in the development of an acrylic elastomer called Lactoprene-EV, which could be vulcanized to a rubber-like material with unusual properties. This elastomer, a copolymer of 95 per cent ethyl acrylate and 5 per cent chloroethylvinyl ether, was vulcanizable with sulfur and organic amines, such as Trimene Base. The vulcanizates showed unusual resistance to heat and hot mineral oils, as well as to atmospheric degradation and flexural breakdown. Commercial modifications, known as Hycar PA-21 and Hycar PA-31, have subsequently become available[2].

More recently another acrylic elastomer, a copolymer of butyl acrylate and acrylonitrile, called Lactoprene-BN, was developed in this Laboratory[3]. This new elastomer showed the desirable heat-resisting properties of Lactoprene-EV; furthermore, the low-temperature properties and the resistance to swelling by boiling water were considerably improved over those of Lactoprene-EV.

This paper reports the preparation of Lactoprene-BN, the butyl acrylate-acrylonitrile copolymer, as well as other acrylate-acrylonitrile copolymers. A preliminary evaluation of the heat stability and the temperature of embrittlement of the vulcanizates is also reported.

PREPARATION OF POLYMERS

Emulsion polymerization.—The method of emulsion polymerization was, in general, similar to that described previously[4]. The preparation of the butyl acrylate-acrylonitrile copolymer, described below, is typical.

The acrylate monomer was purified by vacuum distillation in the presence of hydroquinone, and the redistilled monomer was freed of traces of hydroquinone by washing with cold dilute sodium hydroxide, followed by washing with water to remove alkali. The commercial grade acrylonitrile was distilled at atmospheric pressure.

The polymerization charge was as follows: monomer, 100 parts; distilled water, 200 parts; emulsifier, 1–2 parts; and potassium persulfate, 0.02–0.03 part. Water and the emulsifying agent were charged into a three-necked flask fitted with a stirrer, reflux condenser, and thermometer. The monomer mixture was added, with continuous stirring, and the flask was heated by steam until the temperature of the contents was about 70° C. Then 0.01 part of potassium persulfate was added, and heating continued. When the temperature of the charge reached approximately 87–91° C, vigorous polymerization

* Reprinted from *The Rubber Age* of New York, Vol. 72, No. 11, pages 631–637, February 1953.

set in. At this stage, heating with steam was discontinued and the reaction was kept under control by periodically cooling the flask with a stream of tap water. Even with as large a batch as 3000 grams of monomer, proper intermittent cooling permitted polymerization to proceed under reflux at a high rate, but still under control.

When vigorous polymerization had subsided (after approximately one-half hour), an additional 0.01 part of potassium persulfate was added, and the reaction was heated again by steam. This additional catalyst usually produced a further mild polymerization. A third 0.01 part of potassium persulfate was added after another one-half hour. The temperature of the refluxing emulsion generally rose to approximately 98° C, indicating almost complete polymerization. The temperature of the refluxing mixture was a valuable aid in following the course of polymerization, gradually increasing as monomer was consumed. Sampling of the polymerization mixture, as described under "Redox Polymerization," provided data for the approximate conversion curve (Figure 1), from

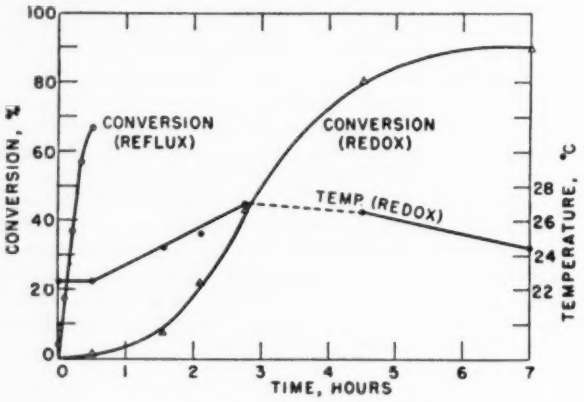


FIG. 1.—Conversion curves for the polymerization of 87.5 per cent butyl acrylate-12.5 per cent acrylonitrile.

which it can be seen that approximately 70 per cent of the monomer is converted to polymer in one-half hour.

When an attempt was made to prepare an emulsion containing 50 per cent solids (87.5 per cent butyl acrylate —12.5 per cent acrylonitrile copolymer), considerable difficulty was encountered with foaming. Furthermore, the emulsion thickened so much that stirring was ineffective. The preparation of a 40 per cent solids latex, however, was not so difficult, although considerable foaming occurred.

Unreacted monomer was next removed from the emulsion by passing live steam into the emulsion. During this stripping of monomer, the flask was heated externally by steam to minimize lowering the solids content by condensation. The emulsion was then broken by pouring it into an equal volume of 0.25 per cent aluminum sulfate solution at approximately 50° C. The copolymer usually separated as a nice white granular material, which was thoroughly washed and finally dried at 50–55° C in a circulating air oven. Some copolymers, particularly copolymers of the acrylic esters higher than butyl,

TABLE I

PREPARATION OF BUTYL ACRYLATE–ACRYLONITRILE COPOLYMER (LACTOPRENE–BN)

Co-polymer no.	Monomers (wt.-%)		Emulsifiers (%)[a]	$K_2S_2O_8$ (%)[a]	Temp. (° C)[b]	Time (hrs.)	Polymer		% Nitrogen in		Intrinsic viscosity[c]
	Butyl acrylate	Acrylo-nitrile					Con-version (%)	Yield (%)	Poly-mer	Mono-mer charge	
1	95.0	5.0	Dupanol-ME, 1	0.03	91–98.5	3.8	94	97	1.10	1.32	Insol.
2	90.0	10.0	Dupanol-ME, 1	0.03	89–98.5	2.4	96	99	2.35	2.64	Insol.
3	85.0	15.0	Dupanol-ME, 1	0.02	87–96	5.0	91	96	3.33	3.96	4.68
4	75.0	25.0	Dupanol-ME, 1	0.03	83–96	3.0	96	101	6.24	6.60	Insol.
5	87.5	12.5	Dupanol-ME, 1	0.03	88–98	2.8	94	98	2.75	3.30	4.81
6[d]	87.5	12.5	Dupanol-ME, 1	0.02	91–98.5	5.7	89	95	2.86	3.30	3.38
7[e]	87.5	12.5	Dupanol-ME, 0.5	0.03	88.5–96	2.8	83	91	2.54	3.30	4.10
8	87.5	12.5	Na stearate, 2	0.06	90–97	2.0	71[f]	65[f]	3.07	3.30	2.35
9	87.5	12.5	Triton-720, 2	0.03	87–95	2.0	89	96	2.81	3.30	Insol.
10	87.5	12.5	Triton-720, 1 Tergitol paste No. 4, 1	0.05	88.5–97	2.5	92	97	3.01	3.30	Insol.
11[g]	87.5	12.5	Dupanol-ME, 2	Redox	22.5–27	7.0	91	91	2.46	3.30	Insol.

[a] 100% solids, based on monomer; catalyst added in separate portions of 0.01%. [b] Initial and final temperature of refluxing polymerization mixture. [c] In acetone at 28° C. Insol. denotes presence of a gel component. [d] A semicontinuous polymerization. Monomers fed in one stream; H_2O, emulsifier, and $K_2S_2O_8$ (0.01%) fed in the other, over a period of 2.5 hours. Conversion at end of this stage was 73%. Heating with additional 0.01% $K_2S_2O_8$ increased conversion to 89%. [e] Polymerization carried out in stainless steel vessel with brass and copper fittings. [f] Some loss of monomer during vigorous portion of polymerization. [g] Redox polymerization under nitrogen. Initiated by 0.06% $K_2S_2O_8$ and 0.03% $NaHSO_2$.

TABLE II

PREPARATION OF ACRYLIC ESTER–ACRYLIC NITRILE COPOLYMERS[a]

Co-polymer no.	Monomers (wt.-%)		Temp.[b] (° C)	Time (hrs.)	Polymer: Conversion, (%)	Polymer: Yield, (%)	% Nitrogen in: Polymer	% Nitrogen in: Monomer charge	Intrinsic viscosity[c]
12	Ethyl acrylate, 95	Acrylonitrile, 5	82–99	1.4	95	97	1.29	1.32	6.69
13	Ethyl acrylate, 90	Acrylonitrile, 10	82–96.5	1.7	93	97	2.51	2.64	5.98
14	n-Propyl acrylate, 95	Acrylonitrile, 5	85–97	3.3	95	97	1.35	1.32	Insol.
15	n-Butyl acrylate, 95	Methacrylonitrile, 5	92–98	1.5	95	96	1.05	1.04	Insol.
16	n-Butyl acrylate, 85	Methacrylonitrile, 15	93–99.5	5.0	93	94	2.98	3.13	2.73
17	n-Amyl acrylate, 95	Acrylonitrile, 5	94–97	3.5	89	93	1.28	1.32	Insol.
18	n-Hexyl acrylate, 91	Acrylonitrile, 9	87–96	3.5	81	96	1.69	2.38	Insol.
19	n-Hexyl acrylate, 90[d]	Acrylonitrile, 10[d]	20–30[d]	5.8	96	98	2.03	2.64	3.67
20	n-Octyl acrylate, 90	Acrylonitrile, 10	91–97	3.5	96	98	2.11	2.64	Insol.
21	n-Octyl acrylate, 85	Acrylonitrile, 15	88–97	2.4	95	97	3.54	3.96	Insol.
22	n-Octyl acrylate, 80	Acrylonitrile, 20	83–97	4.0	90	94	4.88	5.28	Insol.
23	2-Ethylhexyl acrylate, 90	Acrylonitrile, 10	86–97.5	1.8	94	—	—	2.64	—
			Terpolymers						
24	Ethyl acrylate, 10 Butyl acrylate, 80	Acrylonitrile, 10	89–97	2.5	90	97	2.36	2.64	3.00
25	Ethyl acrylate, 20 Butyl acrylate, 70	Acrylonitrile, 10	87–98	2.3	93	98	2.37	2.64	4.95
26	Ethyl acrylate, 40 Butyl acrylate, 50	Acrylonitrile, 10	84–98	3.5	93	97	2.32	2.64	5.27
27	Ethyl acrylate, 10 n-Octyl acrylate, 80	Acrylonitrile, 10	88–97	2.5	94	—	2.40	2.64	Insol.
28	Ethyl acrylate, 20 n-Octyl acrylate, 70	Acrylonitirle, 10	86–98	3.0	94	—	2.45	2.64	Insol.
29	Ethyl acrylate, 30 n-Octyl acrylate, 60	Acrylonitrile, 10	84–97	4.0	95	—	2.47	2.64	Insol.

[a] 1% Dupanol ME and 0.02–0.03% $K_2S_2O_8$ (based on monomer), except Copolymers 15, 16, and 17, in which 0.05% $K_2S_2O_8$ was used, and Copolymer 19 (footnoted). [b] Initial and final temperature of refluxing polymerization. [c] In acetone at 28° C. Insol. denotes presence of a gel component. [d] Redox polymerization under nitrogen with 0.06% each of $K_2S_2O_8$ and $NaHSO_3$ followed by an additional 0.06% each after 2.5 hours.

separated as a spongy mass; however, this was easily washed and shredded. Often when the polymer tended to precipitate as one large mass, this was prevented by adding about 1 gram of Dupanol-ME to the aluminum sulfate solution prior to the addition of the emulsion. Table I summarizes the preparation of various butyl acrylate-acrylonitrile copolymers (Lactoprene-BN). Table II summarizes the preparation of other acrylic ester-acrylonitrile copolymers. It can be seen that the yields, based on monomer actually consumed, are almost quantitative.

Reduction activation (Redox) polymerization in emulsion.—The recipe used was 350 grams of butyl acrylate, 50 grams of acrylonitrile, 800 cc. of distilled water, 8 grams of Dupanol-ME, 0.24 gram of potassium persulfate, and a total of 0.12 gram of sodium bisulfite (Copolymer 11, Table I). Potassium persulfate plus sodium bisulfite was first used by Bacon[5] as a reduction-activation system to polymerize acrylonitrile. All the ingredients except the bisulfite were charged into a flask immersed in tap water (approximately 23° C). The flask was equipped with stirrer, condenser, thermometer, and a nitrogen inlet tube; a stopcock sealed to the bottom of the flask facilitated sampling of the polymerization mixture. Nitrogen was then passed into the flask, and after 10 minutes 0.06 gram of sodium bisulfite was added. Forty minutes later an additional 0.06 gram of sodium bisulfite was added.

Seventy minutes after the first addition of bisulfite, polymerization began. It occurred smoothly, and no great evolution of heat was noted. The polymerization, which was followed by periodically withdrawing samples of the emulsion into a stopping solution of 1 per cent hydroquinone and evaporating to dryness (Figure 1), appeared to be completed after 7 hours. The emulsion was then steam-distilled. Only 3 grams of monomer was recovered. The polymer was obtained by pouring the latex into 0.25 per cent aluminum sulfate. After drying, 362 grams (91 per cent yield) of polymer was obtained.

A hexyl acrylate-acrylonitrile copolymer was also prepared by redox polymerization (Copolymer 19, Table II).

VULCANIZATION OF POLYMERS

These copolymers were relatively free of tack and were readily handled in the conventional rubber compounding equipment. As with Lactoprene-EV, no initial breakdown was required. In general, the vulcanization procedure was similar to that described previously for Lactoprene-EV[6] and Lactoprene-BN[3]. The copolymer was masterbatched with carbon black and stearic acid in a hot Banbury mixer. Sulfur and triethylenetetramine were added on the mill. The recipes shown in Table III were evaluated in this study. The compounded stocks were aged for only 2 hours before curing at 298° F for 60 minutes. A mold release agent was generally used to overcome any tendency to adhere to the mold.

EVALUATION OF VULCANIZATES

The tensile tests were conducted according to ASTM specification D412-41; the die used was similar to die D except that the reduced section of the specimen was $\frac{1}{4}$ inch wide. The brittle points of the vulcanizates were determined by the method of Selker, Winspear, and Kemp[7]. To determine the heat-aging characteristics of these vulcanizates, specimens were heated for 72 hours at 350° F in a mechanical convection oven.

TABLE III

RECIPES USED FOR EVALUATION STUDIES

Recipe[a]	A	B	C	D	E	F	G	H	I	J	K	L
Copolymer	100	100	100	100	100	100	100	100	100	100	100	100
Carbon black (Furnex)	50	50	50	50	50	50	50	50	50	50	50	50
Carbon black (Philblack-O)	—	—	—	—	—	—	—	—	—	—	—	—
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1
Sulfur	0	0	1	0.5	0.25	0.75	0.5	0.5	0.5	1	1	1
Triethylenetetramine	1	2	0.5	0.5	1	0.75	1	1.5	2	1	1.5	2

Recipe[a]	M	N	O	P	Q	R	S	T	U	V	W
Copolymer	100	100	100	100	100	100	100	100	100	100	100
Carbon black (Furnex)	50	50	50	50	50	50	50	—	—	—	—
Carbon black (Philblack-O)	—	—	—	—	—	—	—	50	50	50	50
Stearic acid	1	1	1	1	1	1	1	1	1	1	1
Sulfur	1	2	3	4	5	3	4	1	1	1	1
Triethylenetetramine	2.5	1	1	1	1	1.5	2	1	1.5	2	2.5

[a] Ingredients given in parts by weight.

DISCUSSION OF RESULTS

Polymerization.—Copolymerization with acrylonitrile of the acrylates through butyl proceeded vigorously. In the higher acrylates, the rate of polymerization was noticeably more moderate. Increasing the acrylonitrile content of the monomer charge also resulted in moderation of the rate of polymerization. Copolymerization of butyl acrylate with methacrylonitrile (Copolymers 15 and 16, Table II) was considerably slower than the copolymerization with acrylonitrile. More catalyst, approximately 0.04 per cent, was required to initiate the polymerization, and cooling was not necessary after polymerization began. Conversion to polymer, however, was equally as good as with acrylonitrile. With a few exceptions, more than 80 per cent of the acrylonitrile in the monomer charge entered into the polymer.

The polymerization could be satisfactorily conducted in a stainless steel vessel (Copolymer 7, Table I). Polymerization was also conducted on a semicontinuous basis by feeding the monomer in one stream and the aqueous phase, containing emulsifier and persulfate, in another stream (Copolymer 6, Table I). The two streams were fed to a flask heated by steam and containing a stirrer, condenser, and thermometer. By operation in this manner, the polymerization was conducted almost automatically and with no difficulty of control. The redox polymerizations also were characteristically mild.

Tensile properties.—The initial tensile properties of the various vulcanizates are shown in Tables IV to VII. The tensile strengths were significantly lower than those of many butadiene stocks; however, the tensile strengths of most of these stocks were well above a serviceable minimum. The vulcanizates of the butyl acrylate copolymers (Tables IV and V) had substantially higher tensile strengths than octyl acrylate copolymers of comparable acrylonitrile content (Table VI). Increasing the acrylonitrile content of the copolymers appeared to increase the tensile strength (Table V); however, this did not appear to be true in the isolated example of the methacrylonitrile copolymer (Copolymers 15 and 16, Table VII).

In general, the tensile strengths decreased as the alkyl group of the acrylic ester increased. From previous experience and experiments with Copolymer No. 1 (Table V) and Copolymer No. 19 (Table VII), it is concluded that the tensile strengths can be substantially increased by replacing the Furnex with Philblack-O. The tensile strengths of the copolymers of the higher acrylates, particularly octyl acrylate, were increased by replacing part of the higher acrylate with ethyl acrylate (Copolymers 27, 28, 29, Table VI). Compared with the ethyl acrylate-acrylonitrile and butyl acrylate-acrylonitrile copolymers, lower tensile strengths were shown by the copolymers of amyl, hexyl, *n*-octyl, and 2-ethylhexyl acrylates with acrylonitrile and by the butyl acrylate-methacrylonitrile copolymer. The hexyl acrylate-acrylonitrile copolymer, prepared by redox polymerization, when loaded with Philblack-O gave vulcanizates with tensile strengths as high as those of the butyl or ethyl acrylate copolymers. Thus it appears evident that, by suitable compounding, these copolymers produce vulcanizates with tensile strengths sufficiently high for many applications.

The tables show that the state of cure can be significantly altered by changes in the amine-sulfur ratio. In general, high amine concentrations result in vulcanizates with low elongations and fairly high hardness values. A minimal concentration of sulfur is necessary for the desired heat resistance; however, high sulfur concentrations apparently contribute little to the tensile properties of

TABLE IV

LACTOPRENE BN–12.5 COPOLYMERS[a]

Copolymer No.[b]	Raw Mooney	Vulcanizate[c]	Initial properties: Tensile strength (lb. per sq. in.)	Initial properties: Ultimate elongation (%)	Initial properties: Modulus at 200% (lb. per sq. in.)	Initial properties: Hardness[i]	Initial properties: Brittle point (° F)	Aged 72 hrs. at 350° F: Tensile strength (lb. per sq. in.)	Aged 72 hrs. at 350° F: Ultimate elongation (%)	Aged 72 hrs. at 350° F: Modulus at 100% (lb. per sq. in.)	Aged 72 hrs. at 350° F: Hardness[i]	Aged 72 hrs. at 350° F: Brittle point (° F)
8[d]	37.5	J	1240	490	480	52	−11	1110	180	580	71	− 6
		K	1390	400	670	55	− 9	1150	150	750	75	0
		L	1330	200	1330	71	—	1340	80	0	86	—
		M	1360	180	—	73	—	1440	80	—	89	—
10[e]	37.5	J	1090	360	430	57	− 9	1050	170	530	68	0
		K	1270	260	1000	59	−11	1270	90	—	79	− 2
		L	1250	160	—	67	—	1420	70	—	87	—
		M	1410	170	—	69	—	1490	60	—	89	—
9[f]	39.8	J	1360	330	640	50	−24	1030	150	700	68	− 6
		K	1480	300	1000	53	−22	1280	110	1100	73	0
		L	1350	160	—	63	—	1390	90	—	83	—
		M	1400	140	—	68	—	1550	60	—	89	—
11[g]	32.5	J	1230	680	210	38	−27	1000	280	140	48	−22
		K	1380	420	500	44	−27	1050	160	480	61	−18
		L	1360	250	1100	51	−22	1200	110	1140	69	—
		M	1280	110	—	71	−22	1500	60	—	87	—
6[h]	37.5	C				Undercured						
		J	1400	260	1090	52	—	1280	120	1060	70	—
		K	1410	210	1360	59	—	1170	90	—	74	—
		L	1280	110	—	70	—	1580	60	—	86	—
5	34.0	C	900	560	190	35	—	1180	420	1506	42	—
		J	1340	390	510	45	−22	1400	210	540	59	—
		K	1260	190	—	58	—	1340	90	—	76	—
		L	1190	150	—	61	—	1390	80	—	79	—
7	37.8	C				Undercured						
		J	1280	300	690	50	−13	1140	140	660	63	—
		K	1150	200	1150	55	—	1190	100	1190	72	—
		L	1200	130	—	64	—	1330	60	—	83	—

[a] Lactoprene BN-12.5 is the copolymer prepared from a monomer charge of 87.5% butyl acrylate and 12.5% acrylonitrile. [b] Copolymer number corresponds to number of the polymer in Tables I and II. [c] Cures for 60 min. at 298° F. [d] Copolymer was prepared with Na stearate as emulsifier. [e] Triton-702 and Tergitol Paste No. 4 were used as emulsifiers in the polymerization. [f] Triton-720 was the emulsifying agent in preparing the copolymer. [g] Redox copolymer. [h] Semicontinuous polymerization. [i] Shore Durometer A.

Table V

Other Butyl Acrylate Copolymers and Terpolymers

Copolymer No.[a]	Monomer charge	Raw Mooney	Vulcanizates[b]	Initial properties: Tensile strength (lb. per sq. in.)	Initial properties: Ultimate elongation (%)	Initial properties: Modulus at 200% (lb. per sq. in.)	Initial properties: Hardness[d]	Initial properties: Brittle point (° F)	Aged 72 hrs. at 350° F: Tensile strength (lb. per sq. in.)	Aged 72 hrs. at 350° F: Ultimate elongation (%)	Aged 72 hrs. at 350° F: Modulus at 100% (lb. per sq. in.)	Aged 72 hrs. at 350° F: Hardness[d]	Aged 72 hrs. at 350° F: Brittle point (° F)
1[c]	Butyl acrylate-95	—	T	1230	470	470	58	−29	1160	310	410	71	−20
	Acrylonitrile-5		U	1450	340	770	64	−29	1270	210	610	75	−18
			V	1480	250	1190	69	−29	—	—	—	—	—
			W	1490	180	—	73	—	—	—	—	—	—
1[c]	Butyl acrylate-95	—	J	1120	480	380	54	−36	1070	230	300	54	−33
	Acrylonitrile-5		K	1100	270	740	56	−33	870	120	660	63	−27
			L	1020	220	920	60	−31	—	—	—	—	—
			M	730	150	—	63	−33	—	—	—	—	—
2	Butyl acrylate-90	—	G	1360	250	1020	55	−33	1240	140	—	67	—
	Acrylonitrile-10		J	1400	270	990	56	−29	1190	130	—	70	—
			K	1250	190	—	60	−27	1190	100	—	76	—
			N	1395	280	970	56	−26	1290	130	—	71	—
3	Butyl acrylate-85	52.5	D	1380	570	570	47	−17	1360	240	380	46	− 8
	Acrylonitrile-15		G	1640	230	1450	60	−17	1660	100	1660	77	− 9
			H	1450	140	—	69	—	1720	60	—	87	—
			I	1430	90	—	75	—	1760	40	—	92	—
4	Butyl acrylate-75	85.5	D	1880	240	1790	70	+21	2750	80	—	90	+43
	Acrylonitrile-25		G	1960	140	—	78	—	2810	30	—	99	—
			H	2020	100	—	85	—	Too brittle to test				
			I	2100	60	—	92	—	Too brittle to test				
24	Butyl acrylate-80	35.5	C	910	840	180	34	—	1070	550	130	41	—
	Ethyl acrylate-10		J	1280	390	550	48	−22	1160	200	400	56	−11
	Acrylonitrile-10		K	1150	170	—	59	—	1210	90	0	71	—
			L	1120	140	—	60	—	1140	70	—	77	—
25	Butyl acrylate-70	—	C	Undercured									
	Ethyl acrylate-20		J	1300	380	550	47	−20	1260	180	500	60	—
	Acrylonitrile-10		K	1190	240	930	55	—	1200	120	980	71	—
			L	1150	150	—	60	—	1280	80	—	80	—
26	Butyl acrylate-50	—	C	Undercured									
	Ethyl acrylate-40		J	1420	420	540	48	− 8	1380	210	500	60	—
	Acrylonitrile-10		K	1350	240	1090	57	—	1360	110	1310	74	—
			L	1230	150	—	65	—	1370	70	—	85	—

[a] Copolymer number corresponds to the number of the polymer in Tables I and II. [b] Cured for 60 min. at 298° F. [c] The same copolymer was used with different carbon blacks. [d] Shore Durometer A.

TABLE VI

OCTYL ACRYLATE COPOLYMERS AND TERPOLYMERS

Copolymer No.[a]	Monomer charge	Vulcanizate[b]	Initial properties: Tensile strength (lb. per sq. in.)	Initial properties: Ultimate elongation (%)	Initial properties: Modulus at 200% (lb. per sq. in.)	Initial properties: Hardness[c]	Initial properties: Brittle point (° F)	Aged 72 hrs. at 350° F: Tensile strength (lb. per sq. in.)	Aged 72 hrs. at 350° F: Ultimate elongation (%)	Aged 72 hrs. at 350° F: Modulus at 200% (lb. per sq. in.)	Aged 72 hrs. at 350° F: Hardness[c]
20	n-Octyl acrylate-90 Acrylonitrile-10	A	Undercured								
		J	880	270	600	47	−51	390	70	—	66
		B	800	440	210	35	—	Too brittle to test			
		L	730	130	—	60	—	600	50	—	79
		G	760	420	370	44	−44	360	90	—	65
21	n-Octyl acrylate-85 Acrylonitrile-15	E	970	250	740	50	−44	640	60	—	75
		G									
		J	1100	260	780	52	−42	840	70	—	78
		F	960	300	540	43	−44	680	80	—	71
22	n-Octyl acrylate-80 Acrylonitrile-20	E	1300	150	—	65	−26				
		G	1280	150	—	67	−27	Too brittle to test			
		J	1310	130	—	71	—				
		F	1350	170	—	64	−27				
23	2-Ethylhexyl acrylate-90 Acrylonitrile-10	D			Undercured						
		G			Undercured						
		H	430	480	220	35	—	Too brittle to test			
		I	730	130	—	60	—				

TABLE VI—*Continued*

Copolymer No.[a]	Monomer charge	Vulcanizate[b]	Initial properties: Tensile strength (lb. per sq. in.)	Initial properties: Ultimate elongation (%)	Initial properties: Modulus at 200% (lb. per sq. in.)	Initial properties: Hardness[c]	Initial properties: Brittle point (° F)	Aged 72 hrs. at 350° F: Tensile strength (lb. per sq. in.)	Aged 72 hrs. at 350° F: Ultimate elongation (%)	Aged 72 hrs. at 350° F: Modulus at 200% (lb. per sq. in.)	Aged 72 hrs. at 350° F: Hardness[c]
27	n-Octyl acrylate-80	A	610	570	150	30	—		Too brittle to test		
	Ethyl acrylate-10	B	630	310	300	37	—		Too brittle to test		
	Acrylonitrile-10	J	950	370	440	45	−44	460	90	—	65
		L	950	220	870	54	—	600	70	—	75
		G	930	310	550	48	−44	390	70	—	70
28	n-Octyl acrylate-70	A	580	700	150	32	−35	250	70	—	61
	Ethyl acrylate-20	J	990	340	290	45	−33	560	110	550	63
	Acrylonitrile-10	B	650	460	210	35	—		Too brittle to test		
		L	990	110	—	67	—	790	30	—	85
		G	990	260	730	52	−33	390	30	—	70
29	n-Octyl acrylate-60	C			Undercured						
	Ethyl acrylate-30	J	1190	360	580	47	−31	770	100	770	71
	Acrylonitrile-10	K	1200	200	1200	59	—	910	50	—	81
		L	1180	120	—	68	—	1290	40	—	90
		N	1130	320	600	51	−24	750	90	—	75
		O	1070	340	580	51	—	840	80	—	75
		P	1110	350	600	50	—	840	80	—	75
		Q	1150	350	580	50	—	860	80	—	75
		A	690	590	250	40	—		Too brittle to test		
		G	1230	240	990	56	−24	800	70	—	77
		R	1290	140	—	75	—	1290	50	—	90
		S	1290	90	—	81	—	1300	30	—	96

[a] Copolymer number corresponds to number of the polymer in Tables I and II. [b] Cured for 60 min. at 298° F. [c] Shore Durometer A.

TABLE VII

MISCELLANEOUS ACRYLIC COPOLYMERS

Copolymer No.[a]	Monomer charge	Raw Mooney	Vulcanizates[b]	Initial properties: Tensile strength (lb. per sq. in.)	Ultimate elongation (%)	Modulus at 200% (lb. per sq. in.)	Hardness[d]	Brittle point (° F)	Aged 72 hrs. at 350° F: Tensile strength (lb. per sq. in.)	Ultimate elongation (%)	Modulus at 100% (lb. per sq. in.)	Hardness[d]	Brittle point (° F)
13	Ethyl acrylate-90 Acrylonitrile-10	58.6	C	1410	510	630	52	—	1400	440	580	62	—
			J	1540	310	1060	57	+27	1650	150	1290	77	+43
			K	1550	230	1390	60	+30	1950	90	—	84	+43
			L	1630	150	—	70	—	2440	60	—	94	—
12	Ethyl acrylate-95 Acrylonitrile-5	48.3	C	Undercured									
			J	1410	480	470	49	+16	1510	300	440	60	+25
			K	1400	300	830	56	+18	1520	150	1000	71	+27
			L	1360	210	1280	59	—	1590	110	1420	75	—
17	Amyl acrylate-95 Acrylonitrile-5	22.8	J	730	360	340	36	−45	610	200	140	41	−38
			K	760	300	430	39	−45	680	180	230	48	−42
			L	820	270	600	41	—	730	150	430	53	—
			M	400	140	—	46	—	760	110	540	62	—
18	Hexyl acrylate-91 Acrylonitrile-9		J	790	430	240	43	−49	280	100	280	56	−15
			K	740	200	740	56	—	800	110	750	67	—
			L	940	170	—	61	—	870	90	—	74	—
			L[c]	870	170	—	60	—	—	—	—	—	—
19[d]	Hexyl acrylate-90 Acrylonitrile-10		T	910	670	260	55	—	970	330	290	74	—
			U	1410	390	680	64	—	1110	150	780	84	—
			V[c]	1540	220	1390	74	—	1200	80	—	91	—
15	Butyl acrylate-95 Methacrylonitrile-5	24.0	J	Undercured									
			K	730	490	210	32	−36	690	360	30	37	−36
			L	760	480	230	36	−34	670	300	70	44	−31
			M	830	270	580	41	—	750	170	370	59	—
16	Butyl acrylate-85 Methacrylonitrile-15	28.0	J	450	600	340	45	− 9	530	300	380	62	− 6
			K	580	340	510	60	− 2	590	160	500	82	− 2
			L	700	270	620	68	—	670	130	610	87	—
			M	720	180	—	81	—	750	100	750	94	—

[a] Copolymer number corresponds to the number of the polymer in Tables I and II. [b] Cured for 60 min. at 298° F. [c] Cured for 30 min. at 298° F. [d] Redox copolymer.
[d] Shore Durometer A.

the vulcanizates. This is best illustrated by the vulcanizates of Copolymer No. 29 (Table VI). Vulcanizate J contained one part of triethylene tetramine and one part of sulfur. Holding the amine concentration to one part and increasing the sulfur concentration stepwise to 5 parts (Vulcanizates N, O, P, and Q) gave vulcanizates that had similar tensile properties.

Brittle points of the vulcanizates.—The bend-brittle points of the green stocks (Tables IV to VII), were determined as described by previous investigators[7]. The brittle point depends on the polymer composition, increasing with higher acrylonitrile content and decreasing with the copolymers of the higher acrylic esters. The ethyl acrylate-acrylonitrile vulcanizates had brittle points from +16° F (for the copolymer prepared from a monomer mixture of 95 per cent ethyl acrylate and 5 per cent acrylonitrile) to about +30° F (for the copolymer prepared with 10 per cent acrylonitrile) (Copolymers 12, 13, Table VII).

The brittle points of the copolymers of the higher acrylates are lower, but depend on the acrylonitrile content of the copolymer, which is largely dependent on the acrylonitrile content of the monomer charge and to a less extent on the polymerization conditions. For example, a copolymer prepared from 95 per cent butyl acrylate and 5 per cent acrylonitrile (Copolymer No. 1, Table V) had a brittle temperature of about —33° F. The copolymers from a monomer mixture of 87.5 per cent butyl acrylate and 12.5 per cent acrylonitrile (Table IV) had on the average brittle points of about —11° F. These values were fairly independent of state of cure. Occasionally samples prepared with this same monomer composition had substantially lower brittle points. Thus, Copolymer Nos. 9 and 11 (Table IV) had brittle points of approximately —25° F. Chemical analysis indicated that the percentage of nitrogen in these samples was somewhat lower than in the other batches. Other copolymers, which have been expressly prepared with the least rise in temperature, also showed lower nitrogen values and, therefore, lower brittle points.

These observations suggest that the chemical composition of the copolymer has a more pronounced effect on the brittle point than structural variations such as branching within the copolymers.

Heat resistance characteristics.—The resistance of acrylic rubbers to dry heat is now well known. The stress-relaxation studies of Tobolsky and coworkers[8] showed that heat resistance depends on two reactions—cross-linking and chain scission—which may occur simultaneously. Heat resistance therefore depends on the rates of these competing reactions. With acrylic vulcanizates, the heat resistance also depends on the vulcanizing ingredients. Dietz, Mast, Dean, and Fisher[6] demonstrated the importance of the compounding ingredients in achieving maximum heat resistance.

Since the change of the tensile properties is rather small when the vulcanizates are exposed to dry heat at 300° F for periods less than one week, they were exposed to higher temperatures to demonstrate the effects of the compounding ingredients and the various acrylic ester copolymers on the heat resistance. In this Laboratory, it is customary to evaluate the tensile properties of vulcanizates that have been exposed to dry heat for 72 hours at 350° F. If the tensile strength does not materially change and the ultimate elongation is above 100 per cent, the vulcanizate is considered to have good dry-heat resistance. This was used as a criterion in comparing the dry-heat resistance of the various acrylic rubbers studied in this investigation.

The heat resistance data presented in Tables IV, V, and VII show that the acrylic vulcanizates had good heat resistance. The tensile properties of the

ethyl through hexyl acrylate-acrylonitrile copolymers demonstrated that the amine-sulfur recipe controls the properties of the aged vulcanizates. The higher the concentration of triethylene tetramine in the recipe, the tighter was the initial state of cure and the state of cure in the aged samples. The best heat resistance was obtained with the lowest concentration of the triethylene tetramine. Previous studies showed that sulfur is essential for maximum heat resistance; only small concentrations are required, however, and high concentrations of sulfur in the recipe produce no significant improvement over the lower concentrations.

The octyl acrylate-acrylonitrile copolymers did not have as good heat resistance as the lower acrylate ester copolymers. The data in Table VI illustrate the excessive decrease of elongation on exposure to dry heat at 350° F for 72 hours. Replacing part of the octyl acrylate with ethyl acrylate did not materially improve the heat resistance of the vulcanizates, as illustrated in Table VI, Copolymer 29. The composition of the monomer mixture was 60 per cent *n*-octyl acrylate, 30 per cent ethyl acrylate, and 10 per cent acrylonitrile, and none of the recipes yielded a vulcanizate with the heat resistance of the lower acrylate-acrylontrile vulcanizates.

Copolymer Nos. 15, 16, Table VII, show the heat resistance of copolymers of butyl acrylate and methacrylonitrile. The initial tensile strengths are not particularly high which perhaps may be attributed to the method of polymerization. The relatively low raw Mooney values of these copolymers suggest that a substantial amount of low molecular weight components were present, thereby lowering the viscosity of the copolymer and also affecting the tensile strengths of the vulcanizates. The heat resistance was exceptionally good, however, since elongations well above 100 per cent were obtained after exposure to 250° F for 72 hours. Replacing the Furnex carbon black with Philblack-O would substantially increase the initial tensile strengths of the vulcanizates, which would in all probability be retained on heat aging.

Heat-aged brittle points.—In recent years a great deal of emphasis has been placed on the low-temperature characteristics of synthetic rubbers, and considerable effort has been devoted to obtaining elastomers with brittle points well below −70° F. The acrylic rubbers described in this paper did not have particularly low brittle points; however, the brittle points of the heat-aged vulcanizates were sustantially the same as those of the green vulcanizates, on the average being higher by only about 10° F.

Tables IV, V, and VII list the brittle points for many of the stocks aged at 350° F for 72 hours. Apparently the change of the brittle point on aging is a good criterion for heat resistance, since many of the vulcanizates that exhibited the greatest change in brittle points also showed poor heat resistance. In particular, the hexyl acrylate-acrylonitrile copolymer (Table VII, Copolymer No. 18) had a brittle point for the green vulcanizates of −49° F; however, on aging the brittle point changed to −15° F. In addition, the elongation of the vulcanizates also changed markedly on aging.

SUMMARY

Copolymers of various acrylic esters, from ethyl to octyl, with 5 to 15 per cent acrylonitrile or methacrylonitrile, were prepared by refluxing emulsion polymerization and in two instances by redox polymerization. These copolymers were easily vulcanized with sulfur and triethylene tetramine recipes.

Heat-resistant vulcanizates were obtained from the copolymers of acrylonitrile with ethyl, butyl, amyl, and hexyl acrylates and also from the copolymer of methacrylonitrile with butyl acrylate. The octyl acrylate-acrylonitrile copolymers and the octyl acrylate, ethyl acrylate, and acrylonitrile terpolymerse did not show similar heat resistance. Terpolymers obtained from ethyl acrylate, butyl acrylate, and acrylonitrile, however, produced heat-resistant vulcanizates.

The vulcanizates of lowest brittle points were obtained from copolymers of the higher acrylic esters, but regardless of the acrylic ester used, the brittle point was considerably increased with increasing acrylonitrile content of the copolymer. The copolymers from 95 per cent amyl acrylate—5 per cent acrylonitrile and the copolymer of 91 per cent hexyl acrylate—9 per cent acrylonitrile showed brittle points of $-45°$ and $-49°$ F, respectively. In general, the brittle point of heat-resistant stocks did not change by more than approximately 10° F on heat-aging for 72 hours at 350° F.

The butyl acrylate-methacrylonitrile copolymer appeared to have somewhat better heat-aging properties than did the butyl acrylate-acrylonitrile copolymer.

ACKNOWLEDGMENT

The authors are indebted to J. Siciliano and H. C. Fromuth for assistance in the preparation and evaluation of some of the copolymers and to L. R. Ross for the nitrogen analyses of the copolymers.

REFERENCES

[1] Mast, Dietz, and Fisher, *India Rubber World* **113**, 223 (1945); Dietz, Mast, Dean, and Fisher, *Ind. Eng. Chem.* **38**, 960 (1946); Mast, Dietz, Dean, and Fisher, *India Rubber World* **116**, 355 (1947); Mast and Fisher, *Ind. Eng. Chem.* **40**, 107 (1948); U. S. Dept. Agriculture, Bur. Agr. Ind. Chem. AIC-206 (ERRL), **1948**, 17 pp. (processed).
[2] Owen, *Rubber Age* (N. Y.) **66**, 544 (1950); Anonymous, "Hycar Polyacrylic Rubbers", Service Bull. H-6, B. F. Goodrich Chemical Co., Aug. **1950**.
[3] Dietz and Hansen, *Rubber Age* (N. Y.) **68**, 699 (1951); U. S. Dept. of Agriculture, Bur. Agr. Ind. Chem. AIC-302 (ERRL), **1951**, 6 pp. (processed).
[4] Mast and Fisher, U. S. Dept. of Agriculture, Bur. Agr. Ind. Chem. AIC-206 (ERRL), 17 pp., **1948** (processed); Mast and Fisher, *Ind. Eng. Chem.* **41**, 790 (1949).
[5] Bacon, *Trans. Faraday Soc.* **42**, 140 (1946).
[6] Dietz, Dean, and Fisher, *Ind. Eng. Chem.* **38**, 960 (1946).
[7] Selker, Winspear, and Kemp. *Ind. Eng. Chem.* **34**, 157 (1942).
[8] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944).

EFFECT OF CARBON BLACK ON THE DEVELOPMENT OF OXIDATION PROCESSES IN RAW AND VULCANIZED RUBBERS *

A. S. Kuzminskiĭ, L. I. Lyubchanskaya, N. G. Khitrova, and S. I. Bass

Scientific Research Institute of the Rubber Industry, Moscow, USSR

Publications by Rebinder, Ab, and Veĭler[1], Pisarenko and Rebinder[2], and Dogadkin, Pechkovskaya, and Chernikina[3] have been devoted to an explanation of the mechanism of the accelerating action of carbon blacks. However, only fragmentary and contradictory information about the influence of carbon blacks on the development of oxidation processes is found in scientific literature.

In the present article, several important laws regarding the role of channel carbon black in the oxidation of sodium-butadiene rubber are studied.

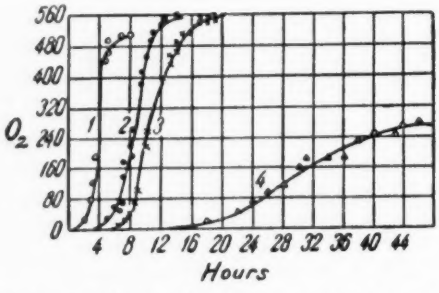


Fig. 1.—Influence of channel carbon black on the kinetics of free oxidation of sodium-butadiene rubber.

1. Oxidation without carbon black
2. Oxidation with 10 parts by weight of carbon black
3. Oxidation with 30 parts by weight of carbon black
4. Oxidation with 50 parts by weight of carbon black

O_2. Quantity of oxygen absorbed in millimoles per moles.

Carbon black can be incorporated in rubber in high proportions (100–125 parts by weight to 100 parts of rubber).

It is well known how great is the influence of the surface area of reaction vessels in which the rupture of chains takes place on the development of chain reactions. It is also known that the oxidation of any type of rubber is a chain process of decomposition, with formation of side chains[4]. Therefore in the study of these processes in rubbers, it is necessary to take into account the highly developed surface of contact between the carbon black and rubber particles.

* Translated for Rubber Chemistry and Technology by Alan Davis from *Doklady Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik*, Vol. 85, No. 1, 131–3 (1952).

Figure 1 shows curves of the kinetics of oxidation of a two-component rubber-carbon black system. Increase of the carbon-black concentration from 10 to 50 parts by weight causes an abrupt slowing down of the reaction. Not only does the speed of the process decrease, but also to a large degree the limit of oxygen absorption.

As has already been shown by Kuzminskiĭ, Degteva, and Lapteva[5], the rate of autocatalytic oxidation of rubbers depends directly on the concentration of stable peroxides. The greater is the latter, the higher is the rate of the reaction.

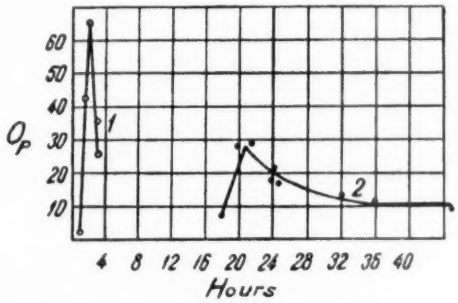


FIG. 2.—Effect of carbon black on accumulation of peroxides during process of oxidation of sodium-butadiene rubber. Temperature—100° C. Loading of carbon black—50 parts by weight.

1. Accumulation of peroxides without carbon black
2. Accumulation of peroxides with carbon black
O_P. Quantity of oxygen in peroxide form in millimoles per mole.

In Figure 2 are seen curves of increase of concentration of peroxides in unloaded rubber and in rubber containing carbon black. In the presence of carbon black, the equilibrium concentration of peroxides decreases at all stages of the reaction. Thus, the inhibiting action of carbon black is associated with decomposition of a part of the peroxides in the rubber on the surface of the carbon black. Not only the stable peroxides, but also the peroxide radicals of the rubber, are destroyed on the surface of the carbon black.

In previous work, Kuzminskiĭ and Lezhnev[6] established that, during the inhibited oxidation of rubbers (in the presence of phenyl-β-naphthylamine), no stable peroxides are formed. The process is controlled by the initiation and

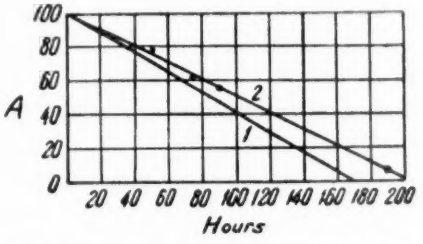


FIG. 3.—Effect of channel carbon black on the rate of consumption of inhibitor in the process of oxidation of sodium-butadiene rubber. Concentration of inhibitor—0.5%. Loading of carbon black—50 parts by weight. Temperature—100° C.

1. Consumption of inhibitor without carbon black
2. Consumption of inhibitor with carbon black
A. Free antioxidant in percentage.

formation of peroxide radicals, which then are decomposed in the reaction with the inhibitor. A special series of experiments showed that the rate of consumption of inhibitor is 23 per cent lower in rubber loaded with carbon black than in unloaded rubber (see Figure 3).

As is seen in Figures 1 and 3, the inhibiting effect of carbon black appears to a much higher degree in autocatalytic oxidation than in the presence of phenyl-β-naphthylamine. This difference of kinetic effects is due to the fact that the destruction of a single peroxide group in the autocatalytic process stops a chain of reactions comprising 6–8 stages, while, during inhibited oxidation, every rupture on the surface of the carbon black causes destruction of only one active center.

The influence of carbon black on the kinetics of oxidation is also revealed by the fact that the part of the inhibitor which is dissolved in the rubber is sorbed and becomes firmly attached to the surface of the carbon black. The

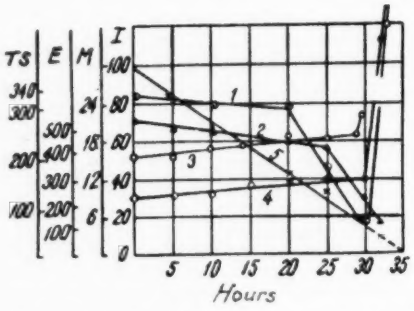


FIG. 4.—Relation of mechanical properties of loaded vulcanizates of sodium-butadiene rubber to time of oxidation at various stages of the reaction. Carbon black, 30 parts by weight. Temperature—130° C.

1. Tensile strength (TS) in kg. per sq. cm.
2. Elongation (E) in percentage
3. Modulus (M_{100}) in kg. per sq. cm.
4. Modulus (M_{300}) in kg. per sq. cm.
5. Free inhibitor (I) in percentage

inhibitor sorbed on the carbon black has no influence on the development of the oxidation process.

Figure 4 shows the consumption of inhibitor and changes of mechanical properties of a vulcanizate of the following composition in parts by weight: sodium-butadiene rubber 100, zinc oxide 2, stearic acid 2, channel carbon black 30, phenyl-β-naphthylamine 0.5, tetramethylthiuram disulfide 2.0. This was vulcanized at 143° C. This vulcanizate was oxidized at 130° C. The critical point in the change of mechanical properties and the development of autocatalytic oxidation are not involved in the resulting exhaustion of all the inhibitor, but only in that part of it which is dissolved in the rubber.

In this unloaded vulcanizate, which contained all the ingredients of the recipe above with the exception of carbon black, this critical point is observed only when no free inhibitor remains in the system. Consequently, the inhibitor, which is sorbed by the carbon black, does not impede the development of the oxidation process. It is necessary to bear in mind that, with an increase of loading of carbon black, the amount of inhibitor sorbed on its surface increases correspondingly.

Only one work, that by Winn, Shelton, and Turnbull[7], has been written about the influence of carbon black on the oxidation of rubber. These authors came to a conclusion diametrically opposed to ours concerning the influence of gaseous channel carbon black on the oxidation of vulcanized rubbers. Winn, Shelton, and Turnbull assert that carbon black not only does not check, but to a large degree catalyzes, the oxidation of vulcanized rubber. They say nothing about what happens to the inhibitors contained in the rubbers they studied.

It is perfectly clear that, by increasing the degree of loading of rubber with carbon black and keeping constant the initial quantity of inhibitors, Winn, Shelton, and Turnbull decreased the effectiveness of the protection of the rubbers. Naturally, therefore, the relative rates of oxidation of the rubbers increased with an increase of the concentration of carbon black. However, this effect is caused, not by the catalytic action of carbon black, as the authors maintain, but by the decrease of the concentration of dissolved inhibitors.

The flaw in the theory of the catalytic action of carbon blacks of Winn, Shelton, and Turnbull[7] is the result of the errors of method indicated above, which render worthless the extensive experimental material.

REFERENCES

[1] Rebinder, Ab, and Veller, *Doklady Akad. Nauk USSR* **31**, 444 (1941).
[2] Pisarenko and Rebinder, *Doklady Akad. Nauk* **40**, 129 (1950).
[3] Dogadkin, Pechkovskaya, and Chernikina, *Kolloid. Zhur.* **8**, 1, 131 (1946).
[4] Kuzminskiĭ, *Zhur. Obshcheĭ Khim.* **18**, 6, 1061 (1948).
[5] Kuzminskiĭ, Degteva, and Lapteva, *Zhur. Fiz. Khim.* **22**, 4, 423 (1949).
[6] Kuzminskiĭ and Lezhnev, *Zhur. Fiz. Khim.* **4**, 5, 539 (1950).
[7] Winn, Shelton, and Turnbull, *Ind. Eng. Chem.* **38**, 10, 1052 (1946).

INFLUENCE OF CARBON BLACK ON THE OXIDATION OF NATURAL RUBBER*

G. J. VAN AMERONGEN

RUBBER-STICHTING, DELFT, HOLLAND

In this investigation an attempt was made to determine to what extent the solubility of oxygen in natural rubber and the aging resistance are influenced by the incorporation of carbon blacks of various particle sizes in the rubber. The influence of the particle size of carbon black on the oxidizability of GR-S loaded with carbon black had already been proved by Winn, Shelton, and Turnbull[1].

In their explanation of this effect, carbon black was considered to be a catalyst for the oxidation reaction of rubber, although nothing was known about the nature of this catalytic action. Moreover, measurements with natural rubber were lacking.

METHODS

The following methods were used in this investigation.

Measurement of the rates of oxidation.—Usually the aging properties of rubber are determined by the Geer Evans oven test or the Bierer-Davis bomb test. These tests, however, give no quantitative data as to the amount of oxygen absorbed during aging. An apparatus was therefore used, with which it was possible to measure the rate of oxidation of 12 small samples of rubber simultaneously. This apparatus, which has been described in detail elsewhere[2], works on the principle of measuring volumetrically the amount of oxygen absorbed during oxidation in an atmosphere of oxygen. During the test the rubber is thermostated at 80° or 110° C, and the oxygen pressure remains virtually constant at 1 atmosphere.

Direct measurement of the solubility of oxygen.—The amount of oxygen which is reversibly absorbed by an amount of finely cut rubber was measured in a specially designed apparatus[3] for measuring the solubility of gases in rubber and consisting of a container connected with a gas volume meter. This physical absorption of oxygen contrasts with the irreversible chemical absorption (oxidation) measured under the first procedure. To avoid chemical absorption as far as possible, these measurements are carried out only at the relatively low temperatures of 25° and 50° C.

Indirect measurement of the solubility of oxygen.—The solubility was calculated[3] from measurements of the permeability and diffusivity of rubber to gases, using the equation:

$$\text{Permeability} = \text{diffusivity} \times \text{solubility}$$

Measurement of the adsorptive power of carbon black.—Iodine adsorption was used to measure the adsorptive power of carbon blacks. One gram of carbon black was shaken for 1 hour with 100 cc. of a 5 per cent potassium iodide solution in which various amounts of iodine had been dissolved. From the adsorp-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 2, pages 377-379, February 1953.

TABLE I

OXIDATION PROPERTIES OF NATURAL RUBBER–CARBON BLACK COMPOUNDS

Carbon black in compound	Surface area (sq. m. per g.)	I_2 adsd., g./g. at 0.2 g. I_2/100 cc. soln.	I_2 adsd., g./g. at 2 g. I_2/100 cc. soln.	O_2 solub. cc./cc. in vulc. compounds		O_2 absd., cc./g./hr. in vulc. compounds				O_2 absd., cc./g./hr. in crepe-black compounds	
				25° C	50° C	80° C., 0–16 hr.	80° C., 16–40 hr.	110° C., 0–4 hr.	110° C., 4–7 hr.	80° C., 16–41 hr.	110° C., 5–21 hr.
Thermax (MT)	19	0.015	0.07	0.088	0.090	0.027	0.021	0.28	0.32	0.011	0.08
P-33 (FT)	21	0.033	0.10	0.098	0.092	0.025	0.022	0.27	0.28	0.015	0.09
Sterling-SO (FEF)	41	0.046	0.13	0.14	0.12	0.032	0.026	0.23	0.39	0.014	0.12
Statex-K (VFF)	75	0.08	0.12	0.19	0.16	0.044	0.033	0.28	0.47	0.019	0.11
Vulcan-3 (HAF)	86	0.083	0.17	0.35	0.25	0.045	0.037	0.35	0.60	0.023	0.14
Spheron-9 (EPC)	106	0.06	0.15	0.61	0.41	0.065	0.047	0.45	0.72	0.035	0.19
Spheron-6 (MPC)	120	0.085	0.16	0.75	0.47	0.075	0.053	0.50	0.66	0.031	0.18
Spheron-4 (HPC)	142	0.09	0.20	0.93	0.58	0.076	0.051	0.46	0.75	0.034	0.18
Voltex (CC)	200	0.20	0.36	0.62	0.47	0.079	0.062	0.54	0.81	0.031	0.24

tion graphs thus obtained, the amount of iodine adsorbed in equilibrium with a 0.2 and 2 per cent iodine solution was determined.

RESULTS

Table I gives a comprehensive survey of results. Measurements were taken with unvulcanized compounds of 100 parts of crepe and 50 parts of carbon black and with vulcanized compounds of 100 parts of crepe, 50 parts of carbon black, 2 parts of sulfur, 5 parts of zinc oxide, 1 part of Santocure, 1 part of stearic acid, and 1 part of phenyl-β-naphthylamine, vulcanized 15 to 20 minutes, depending on the black used, at 142° C.

Column 2 in Table I gives the surface area of the carbon black. These data, which are determined from nitrogen adsorption measurements, are borrowed from the literature[4].

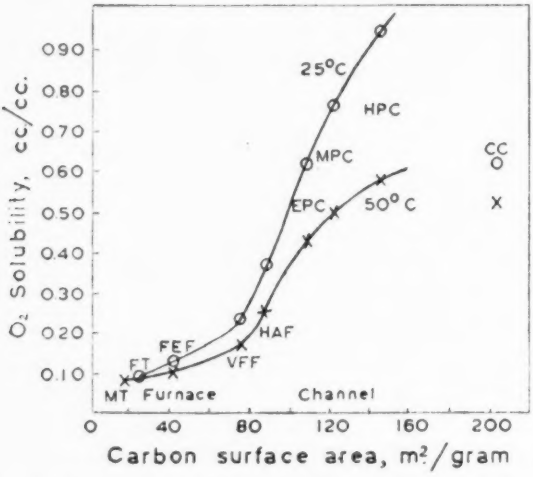


FIG. 1.—Oxygen solubility in natural rubber-carbon black vulcanizates as a function of carbon black surface area.

Columns 3 and 4 give data on iodine adsorption of carbon black in equilibrium with the two concentrations mentioned. Generally this adsorption increases with increasing surface area.

Columns 5 and 6 give results of direct solubility measurements at 25° and 50° C of oxygen in the vulcanized carbon black compounds. The data are expressed in cc. of oxygen at normal temperature and pressure, soluble in 1 cc. of rubber compound at 1 atmosphere oxygen pressure. Calculation of the oxygen solubility from permeability and diffusivity data gave fundamentally the same values. For comparison it should be realized that the solubility of oxygen in a pure-gum vulcanizate at 25° and 50° C is about 0.10 cc. per cc. of rubber or in a compound containing 33 per cent of an inert, nonadsorbing filler, 0.067 cc. per cc. of rubber compound[3].

Figure 1, derived from the data of Table I, shows that the solubility increases very strongly with increasing surface area of the carbon black used.

The concentration of oxygen in a compound containing a very fine black can be 10 times that in a compound containing nonreinforcing blacks. The remarkable point here is that the normal power of carbon black of adsorbing oxygen (or gases in general) is maintained even when mixed with rubber. Apparently carbon black in rubber has still a great amount of free surface, probably in narrow pores, into which the rubber molecules cannot enter.

It is interesting to note that carbon black with a surface area of 100 square meters per gram will adsorb 22.8 cc. of nitrogen per gram of carbon black at −195° C in a monolayer, or 6.0 cc. calculated on the carbon black per ml. of rubber compound[5]. The highest value obtained at 25° C of nitrogen solubility

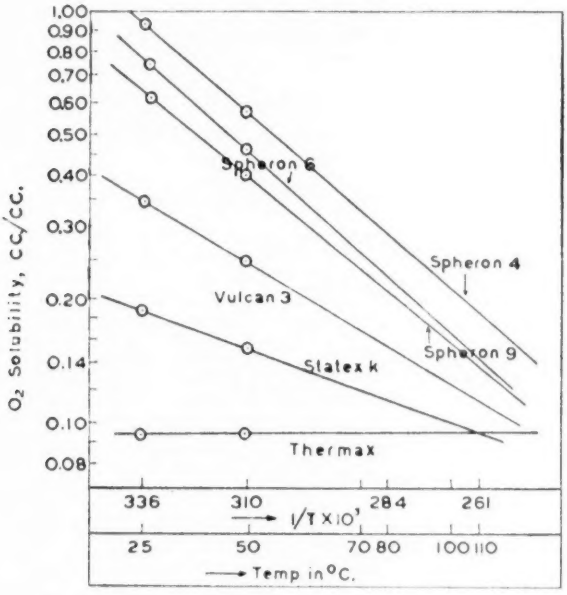


FIG. 2.—Oxygen solubility in natural rubber-carbon black compounds depending on temperature.

in rubber with Spheron-4 loading was 0.61 cc. per cc. of rubber compound, but this will increase considerably on reduction of temperature.

It can be assumed that the dependence of gas solubility, S, on temperature T, follows the equation:

$$\ln S = - H/RT + C$$

where H is the heat of solution and C and R are constants. From this equation it follows that by plotting the oxygen solubility against $1/T$, this solubility can be found at any temperature, *e.g.*, at 70°, 80°, or 110° C (see Figure 2). Oxygen solubilities at these high temperatures cannot be measured directly because of the chemical reaction of rubber and oxygen.

Figure 2 also shows that the difference in oxygen solubility in various carbon black compounds at higher temperatures is considerably less than at lower

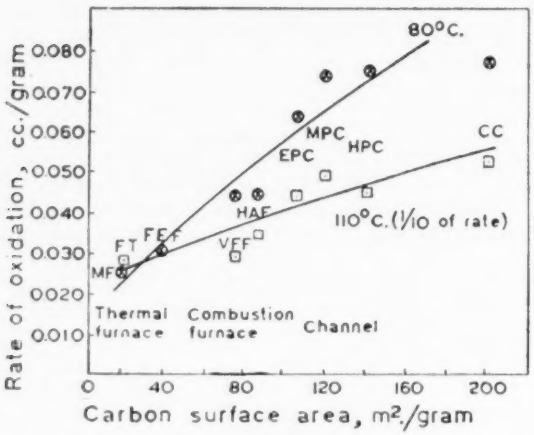


FIG. 3.—Rate of oxidation of natural rubber-carbon black vulcanizates as a function of carbon surface area.

temperatures. In rubber loaded with 50 parts of Spheron-4, for example, 10 times as much oxygen dissolves at 25° C as in the rubber loaded with Thermax. At 110° C, it is only two-fold because of the strong decrease of oxygen solubility, caused by temperature increase. Strongly decreased solubility such as this indicates great heat of solution. Great heat of solution can be interpreted in this case as heat adsorption. The heat of solution of oxygen in the rubber-Spheron 4 and 6 compounds amounts to −3600 calories per moles, in the Spheron-9 compound to −3000 calories per mole, in the Vulcan-3 compound −2600 calories per mole, in the Statex-K compound −1300 calories per mole, and in the Thermax compound +150 calories per mole.

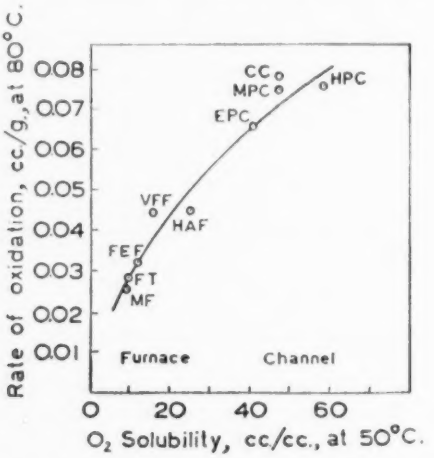


FIG. 4.—Rate of oxidation of natural rubber-carbon black vulcanizates at 80° C as a function of oxygen solubility at 50° C.

Columns 7 to 10 in Table I give the chemical oxygen absorption of vulcanized carbon black compounds at 80° and at 110° C; columns 11 and 12 do the same for the uncured stocks. These data are expressed in cc. of oxygen at normal temperature and pressure absorbed by 1 gram of rubber compound per hour at 1 atmosphere of oxygen pressure. The readings are taken and averaged for a time of oxidation as indicated. Generally the rate of oxidation is slightly dependent on time, being higher at the beginning of the oxidation period and after a long oxidation period. Figure 3, derived from Table I, shows that the rate of oxidation of natural rubber-carbon black vulcanizates increases considerably with increasing surface area of the carbon black used. It is a striking fact that this increase is slower at 110° C. The obvious explanation of this dependence of rate of oxidation on carbon surface area and temperature is that the rate of oxidation is directly related to the oxygen concentration, *i.e.*, oxygen solubility in the rubber, as demonstrated by Figures 1 and 2.

These views are corroborated by Figure 4, which shows that the rate of oxidation depends upon oxygen solubility. Such an increase should be compared with the well-known increase in rate of oxidation on increase of oxygen pressure[6].

DISCUSSION

It is not unlikely that the abrasion properties of rubber are influenced by oxidation processes. It might be suggested that a considerable temperature rise, *e.g.*, of up to 200° to 300° C, will occur locally or on a molecular scale at critical hot spots of a motor-car tire in actual service, *e.g.*, during slippage. In that case breakdown of the rubber under the influence of oxygen and pyrolysis might be important factors in explaining abrasive behavior of motor-car tires.

From this point of view, abrasion might have some factors in common with ordinary mastication of rubber on the mill. It is well known that rubber molecules are broken down on the mill under the influence of mechanical forces (friction) and oxygen at apparently low temperatures, probably because of the local development of hot spots in the rubber.

Even if it is doubted that momentary breakdown is likely to take place during slippage, it is reasonable to assume that evolution of heat at the tire's surface will weaken the rubber in the long run on account of oxidation.

Recognition of the effect of oxidation on abrasion would readily explain the better abrasion properties[7] of furnace blacks in rubber compared with channel blacks (compare Figure 4). In this connection, an explanation of another fact might be suggested. It has been found[7] that tire treads of cold rubber-furnace black compounds sometimes show better resistance to abrasion than natural rubber-furnace black treads. The special circumstances under which this occurs seem to be high temperature and dry weather. Now it might be suggested that one of the reasons for this phenomenon is the greater resistance of cold rubber to high-temperature oxidation. The same argument would of course apply to standard GR-S, but this rubber is obviously inferior on other grounds[8].

Another interesting point is to be learned from Figure 2. It can be imagined that during sudden slippage the temperature of the tire increases locally from 25° to, say, 110° C in a very short time. The oxygen solubility in a rubber with channel black loading should, according to Figure 2, in that case decrease to one fifth of its previous value. If the rate of heating is higher than the rate of

diffusion, this results temporarily in the presence of gas under a pressure five times the normal pressure. Undoubtedly this will have some bearing on oxidation in actual progress[9].

REFERENCES

[1] Winn, Shelton, and Turnbull, *Ind. Eng. Chem.* **38**, 1052 (1946).
[2] Van Amerongen, *Rev. gén. caoutchouc* **20**, 136 (1943); RUBBER CHEM. & TECHNOL. **19**, 170 (1946).
[3] Van Amerongen, *J. Applied Physics* **17**, 972 (1946); RUBBER CHEM. & TECHNOL. **20**, 494 (1947).
[4] Drogin, "Development and Status of Carbon Black", United Carbon Co., Inc., Charleston, W. Va., **1945**; Drogin and Bishop, "Today's Furnace Blacks", United Carbon Co., Inc., Charleston, W. Va., **1947**; Dannenberg and Collier, *Ind. Eng. Chem.* **41**, 1607 (1949).
[5] Beebe, Biscoe, Smith, and Wendell, *J. Am. Chem. Soc.* **69**, 95 (1947).
[6] Van Amerongen, *Rev. gén. caoutchouc* **20**, 136 (1943); RUBBER CHEM. & TECHNOL. **19**, 170 (1946); Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947).
[7] Mandel, Steel, and Stiehler, *Ind. Eng. Chem.* **43**, 2901 (1951).
[8] Fielding, *Ind. Eng. Chem.* **41**, 1560 (1949).
[9] Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947).

THE MICROBIOLOGICAL DETERIORATION OF RUBBER INSULATION *

JOHN T. BLAKE, DONALD W. KITCHIN, AND ORISON S. PRATT

RESEARCH LABORATORY, SIMPLEX WIRE & CABLE CO., CAMBRIDGE, MASS.

Rubber insulated cables buried in the ground without the protection of a metallic sheath are exposed to various hazards that may lead to eventual failure. One type of failure which can be forestalled by proper formulation of compounds is that caused by soil microorganisms.

Research aimed at the development of compounds completely resistant to microorganisms has been in progress for six years. Two major results have been:

1. GR-S compounds that so far appear to possess unlimited life in soil.
2. More exact knowledge of the identity and mode of action of the destructive microorganisms.

In two earlier papers[1] it was established that microbial attack alone can cause drastic loss of insulation resistance in both natural and synthetic rubber insulations. By exposing thin walls of insulation to soil of high microbial activity, failures like those found occasionally after ten or more years in service were produced in a few months. Such a laboratory test, although greatly accelerated, is not unrealistic in the sense that excessive temperature or mechanical or electrical abuse would be. A quick positive test makes it possible to develop truly stable compounds in a reasonable time.

In the standard routine test, 5-foot lengths of 14 solid wire with $\frac{3}{64}$-inch insulation are buried in active soil and the insulation resistance is measured periodically. In this test natural-rubber insulation fails in three to five months, ordinary GR-S insulation in six to nine months. The stable types developed in this work have already maintained normal insulation resistance four years with no failures.

MECHANISMS OF FAILURE

In the earlier papers[1] two distinct types of attack were described:

1. Visible surface pitting.
2. Creation of invisible micropores, with no apparent signs of erosion.

The first type, found only in natural rubber, is much slower than the second, which is common to both natural and synthetic rubber insulation. The existence of these micropores was demonstrated by electrodeposition of copper in the faults. Under the microscope the copper particles could be traced all the way to the conductor. Even natural-rubber insulation was shown by copper deposition to have failed in this way rather than by the slower visible pitting.

These earlier experiments revealed the results of microbial attack, but not the identity of the destructive agents or their actual mode of action.

* Reprinted from the *Transactions of the American Institute of Electrical Engineers*, Vol. 72, pages 321–328 (1953). The paper is also published in *Power Apparatus and Systems*, April 1953, pages 321–328.

The experiments described in this paper show simply and conclusively that the destructive agents are fungi.

These force filaments, or hyphae, through the insulation, presumably following microimperfections which contain foods.

It should be emphasized that, in studying the mechanism of attack, it was necessary to use vulnerable insulations. Such insulations should not be used in underground cables. The stable insulations developed in this work would not have thrown any light on the mode of failure.

THE INHERENT VULNERABILITY OF GR-S AND NATURAL RUBBER INSULATION

The preceding paper[2] pointed out the considerable improvement in stability of GR-S insulation *vs.* microbe attack imparted by improved processing. Thus factory mixing instead of ordinary laboratory mixing prolonged the life of samples with $\frac{3}{64}$-inch walls from four months to about nine months. This raises the interesting question whether it would be possible, in theory at least, to make a relatively nontoxic GR-S insulation completely stable by more perfect processing.

TABLE I

RATE OF FAILURE VERSUS EXPOSED LENGTH OF INSULATION

Sample and exposed length	Per cent of samples failed after						
	3 Months	6 Months	9 Months	11 Months	12 Months	13 Months	48 Months
NR 5 feet	100						
NR 2 inches	92						
GR-S 5 feet	0	8	100				
GR-S 2 inches	0	0	24	75	97	100	
GR-SY 5 feet	0	0	0	0	0	0	0

As a preliminary it was of interest to see whether the imperfections leading to failure were widely separated or more or less uniformly distributed. For this test, factory-run insulation was used, since laboratory-mixed compounds had been shown to contain large numbers of imperfections. The length per sample exposed to soil was limited to two inches by glass tubing over the leads. One hundred GR-S samples and eight of natural rubber were tested. For comparison 5-foot lengths insulated with identical stock of each compound were similarly tested. Table I shows these results, together with those obtained so far with GR-SY, a stable fungitoxic insulation.

This experiment shows that, even when the exposed length is reduced to two inches, no permanently stable region can be found. Thus the imperfections leading to microbiological failure are not merely isolated "accidents", but are inherent in the structure even in factory-run GR-S insulation. If this experiment had been made only with stable fungitoxic GR-S compounds, it would have shown nothing about the distribution of vulnerable regions. Such stable compounds, even when processed in a way that would make ordinary GR-S insulation shortlived, have shown complete stability in soil.

In an attempt to refine the texture still further, factory-mixed stocks of several vulnerable types of insulation were given considerable additional milling at 250° F and allowed to rest overnight before being extruded. This prolonged the time to failure in soil only about 50 per cent.

Since rubber insulation in the form of press-vulcanized sheets is generally believed to possess superior texture, it was of interest to see whether such sheets would resist fungus attack indefinitely or at least much longer than extruded insulation. For this test, 40-mil sheets were clamped between 3-inch pipe tees filled with soil. Mechanical injury was carefully prevented. Exposure of a sheet having soil on both sides is not strictly comparable with that of wire, but this was intended only as a qualitative test.

TABLE II

COMPARISON OF EXTRUDED INSULATION WITH PRESSED SHEETS

Sheet samples	Per cent failed after following time (months)										
	1	2	3	4	5	6	7	9	10	11	12
NR			20	80	100						
GR-S			0	0	0	0	0	0	60		100
GR-SX			0	0	0	67	100				
Extruded samples											
NR			100								
GR-S	0	0	0			0		0		63	
GR-SX	0	25	100								

Three compounds, all of the type having low water absorption, were tested: natural rubber insulation (NR), ordinary GR-S insulation, and an experimental excessively vulnerable GR-S (GR-SX). Table II shows the results.

Compound GR-SX is not manufactured for actual service. It is a useful experimental material, for example, as susceptible insulation for testing Neoprene jackets as fungus barriers, and especially as an aid in studying improvements in processing. Any physical treatment that greatly prolongs the resistance of this compound to fungi could be expected to improve the texture and the quality of GR-S compounds in general. The stable fungitoxic GR-S insulations would be useless for this application.

TABLE III

EFFECT OF PROCESSING ON BUTYL INSULATION

Compound	Per cent of samples failing in			
	12 Months	15 Months	24 Months	30 Months
Butyl *A*	0	0	13	13
Butyl *B*	0	0	0	0
Butyl *C*	0	0	0	0
Butyl *C* (factory)	0	13	25	25

These results and others shown in the preceding paper[2] confirm the belief that neither natural rubber nor GR-S insulations can be made completely resistant against fungus by improved processing alone. To be safe they must be made sufficiently fungitoxic.

Recent results suggest that Neoprene and Butyl compounds possess greater inherent stability against fungus attack, so theoretically they might be made completely fungus-resistant by perfect processing alone. Partial evidence of this was shown in experiments with Neoprene-jacketed latex, described later, where the failures were few and isolated. Similar characteristics are shown by three factory-mixed Butyl compounds, A, B, and C. These were given additional milling in the laboratory and extruded in a laboratory insulator. Eight

samples of each compound were exposed to soil, with eight additional samples of factory-run wire insulated with compound C. The results are given in Table III.

The exposure will have to be carried on much longer to determine whether other weak spots exist. The absence of failures in the laboratory C group shows the improvement resulting from slight additional processing. In spite of the apparent stability of the bulk insulation against fungus attack, it is advisable to guarantee stability by also making the compounds sufficiently fungitoxic.

Polyvinyl chloride and polyethylene samples have all maintained normal insulation resistance for six years. Some silicone compounds have also remained stable in soil for several years.

VARIOUS ENVIRONMENTS

The severity of microbial attack varies greatly with the environment to which insulation is exposed. For example, no failures by fungus attack have occurred in samples kept under water for years, although the water was never sterile.

TABLE IV

DIFFERENCE IN ACTIVITY OF VARIOUS SOILS UNDER LABORATORY CONDITIONS

Soil	Per cent of samples failed after 3 Months	6 Months	9 Months	12 Months
Laboratory test soil	0	67	80	100
Rail yard *A*	0	0	0	50
Rail yard *B*	0	0	0	30

To simulate possible dangerous conditions in wet ducts, ten GR-S samples were dusted lightly with dried soil and placed over water in a closed pail. One had failed after six months, and eight after eleven months.

Samples from this group were used in culture tests described later, which showed that fungi had gone through the wall. Thus, in a humid environment, wire may not only become coated with fungi but may fail because these breach the wall.

TABLE V

INSULATION RESISTANCE AND DIELECTRIC STRENGTH OF GR-S INSULATIONS AFTER 32 MONTHS IN SOIL

Mega-megohms	Alternating volts per mil	Mega-megohms	Direct volts per mil
3.7	276	4.4	468
4.2	284	5.0	516
4.5	91	0.006	262
0.006	82	0.003	163

The difference in virulence of various soils toward rubber insulation was shown by burying samples of an ordinary GR-S insulation in active test soil and in soils from two railroad yards. These soils were kept moist and at room temperature. The results are in Table IV. The difference in sample life was much less than one would expect from the appearance of the soils.

PARALLEL ELECTRICAL AND MICROBIOLOGICAL TESTS

The presence of micropores in failed rubber insulation revealed by electrodeposited copper suggested that some as yet unidentified microorganisms could

actually pass through. This was verified in preliminary experiments in which the conductor was pulled out of wire samples, the resulting tubes filled with nutrient agar, sealed, sterilized, and exposed to soil for about one year. The agar was then squeezed onto culture plates. Abundant fungus growth showed that the agar inside the tubes of the vulnerable types of insulation had become infected by organisms, which must have entered by penetrating the insulation. Such an action would be expected to cause electrical failure. The correlation between fungus penetration and electrical failure was established by rigorous simultaneous electrical and microbiological tests.

The tests of insulation resistance *vs.* soil exposure were made as usual with 5-foot wire samples with $\frac{3}{64}$-inch of insulation of various types. For the microbiological tests, the conductor was pulled out of replicate samples of the same wire.

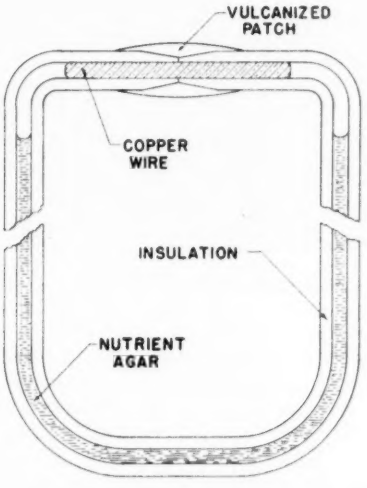


FIG. 1.—Schematic diagram of agar-filled tube of insulation.

The tubes were filled with nutrient agar, sealed by a vulcanized patch of identical insulation over a short stub of copper wire, sterilized 30 minutes in steam at 15 pounds per square inch, and buried in soil. Figure 1 shows the construction. It is evident that any microorganisms found inside after exposure must have passed through the insulation. When samples of any group failed electrically, the corresponding agar-filled tubes were cut and the agar squeezed onto culture plates. As a control test, the agar was also squeezed from exposed tubes of stable insulation. These have invariably given negative results, that is, sterile culture plates.

In any group where there were electrical failures, the culture tests made at the same time showed abundant fungus inside the corresponding tubes. With various compounds, the soil exposure periods on the parallel samples were fourteen, six, and three months, and with an insulation deliberately made excessively vulnerable to soil microbes, although otherwise normal, only one month. Figure 2 shows the petri-dish cultures of agar rods squeezed from tubes of three types of insulation after six months' exposure to soil. The most profuse growth

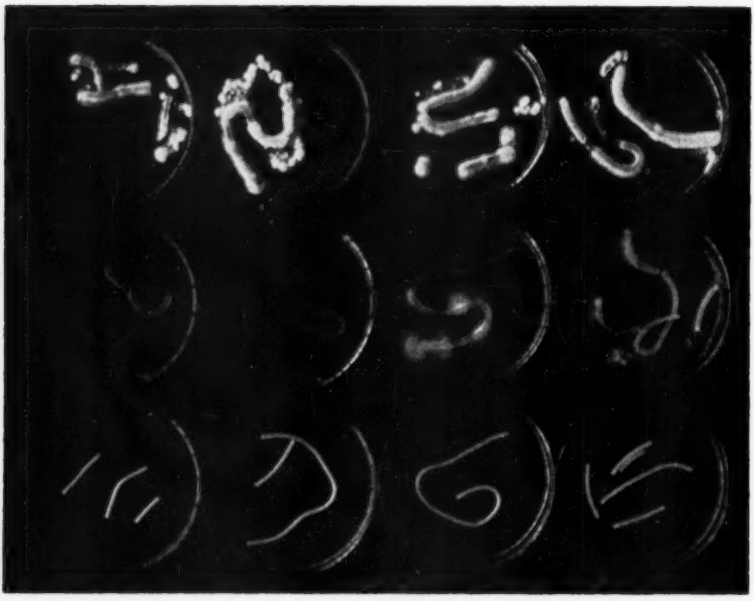


FIG. 2.—Cultures of agar squeezed from tubes of insulation after 6 months in soil. Top row natural rubber, middle row vulnerable GR-S, bottom row stable RG-S.

came from the natural rubber tubes. The middle row shows the organisms from a GR-S insulation very stable in water but not immune to fungi. The completely sterile rods were from GR-S insulation designed to be immune to fungi. In a large number of samples of this insulation there have been no electrical failures during four years of the accelerated laboratory test.

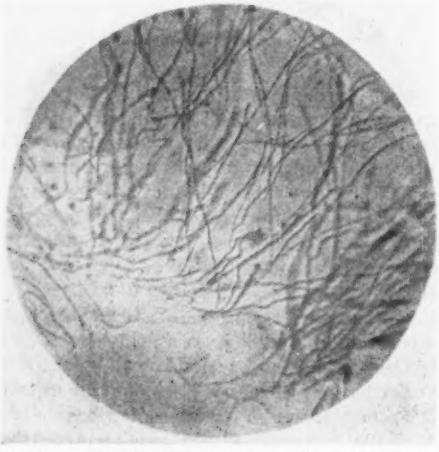


FIG. 3.—Photomicrograph of fungus in agar squeezed from tube of ultravulnerable GR-S insulation after 40 days in soil.

When agar from tubes of insulation was squeezed onto culture plates, it was the usual practice to press some between a cover glass and a slide and examine immediately by microscope to detect fungus hyphae. In any infected portion, the fungus filaments could be seen readily and photographed at a magnification of 100 times. This would afford a quick and convenient test for infection, without the necessity of culturing except that the infected portions are often small and isolated, since the fungi do not spread rapidly lengthwise from the points of entry. When abundant hyphae can be found throughout the extruded agar in a tube sample after short soil exposure, it means that fungi are able to penetrate practically everywhere. Figure 3 shows hyphae in the agar from a tube of the ultravulnerable GR-S after only forty days in soil. The corresponding wire samples had all failed electrically in thirty days. It is evident from the growth that fungus had been present inside for some time before the tube was examined.

Two typical organisms found inside tubes of both natural rubber and GR-S insulation were identified by (Miss) Mary Downing of the Philadelphia Quartermaster Laboratories as Spicaria violacea Abbott and a Fusarium species. In this study the Spicaria also has been the predominant organism found under Neoprene jackets.

The weight of evidence so far indicates that, except for the slow direct eating away of natural rubber, bacteria are not able to effect penetration of the insulation. In some tube samples exposed to soil over periods considerably longer than required for electrical failure, bacteria were found inside. It is believed that these entered only after fungi had breached the wall. No bacterial growth was observed in the tubes exposed six months or less. Some additional evidence that bacteria are not the destructive agents in the microbiological failure of GR-S insulation was given by the following experiment. Wire samples of a GR-S insulation very susceptible to soil exposure were buried in soil in flasks and the whole assembly sterilized. Then the soil was inoculated with a broth culture of a variety of soil bacteria containing no fungi. There have been no failures in this soil in fifteen months, although in the regular soil containing fungi, this insulation normally fails in six months. Since some effective type might be absent, this alone is not conclusive. The most convincing evidence has been the invariable presence of only two or three types of fungi inside tubes in the early stages of failure.

An attempt was made to reverse the usual procedure and observe the emergence of fungus filaments through walls of susceptible GR-S and natural-rubber insulation. Tubes of insulation were immersed in nutrient agar in flasks and the assembly sterilized. Then the tubes were filled with agar heavily inoculated with Spicaria violacea Abbott. Any fungus hyphae which emerged would develop local growth in the outer medium. The effect would be the biological analogue of that in the d-c corona locator described in the earlier paper[2]. Although the particular insulations were of types that fungi could penetrate in three months in the regular soil exposure, no fungus came through in ten months The agar in the tubes was then squeezed onto culture plates. Profuse growth proved that the Spicaria inside was still flourishing. Apparently such an inoculated nutrient medium is less destructive than active soil.

COMBINED ELECTRICAL AND MICROBIOLOGICAL TEST

In the following experiment the separate simultaneous culture and insulation resistance tests were combined by using the same samples for both procedures as follows: After several wire samples of a certain group had failed electrically in

the "duct test" described earlier, the conductor was extracted and the resulting tubes were filled with sterile Sabouraud's agar. This was left in one week, then squeezed out on culture plates. To avoid introducing contaminating organisms, the conductor was stretched, broken in the middle by flexing, and pulled out of the two ends. Two unexposed blanks, two samples that had failed electrically, and one that had not yet failed under identical exposure were thus tested. The blanks and the sample that had not failed during exposure gave completely sterile culture plates. The agar rods squeezed from the two electrically failed samples showed four isolated short infected regions $\frac{1}{4}$ to $\frac{1}{2}$ inch long in several feet of extruded agar rod. The complete sterility of the agar squeezed from the controls and the minute localized infected regions in the agar from the failed samples were convincing evidence that the fungus had entered only through the wall of the failed insulation. The four colonies appeared to be of the same, as yet unidentified, type of fungus.

This method has some obvious advantages. In the earlier separate test with agar-filled tubes there was no direct way, short of destroying the sample, of knowing when fungi had arrived inside. In the combined test, except for controls, samples are given the culture test only after they have failed. The agar can be squeezed out and tested after a few days. There is thus a close and convincing correlation between electrical failure and passage of fungi through the insulation.

DETECTION OF FUNGI IN WALLS OF INSULATION

The insulation resistance test on wire and the culture test on agar-filled tubes both fail to show microbiological deterioration until the wall has been completely penetrated. In the following experiment with exposed wire samples having $\frac{8}{64}$-inch walls of GR-S insulation, it was possible to detect and identify

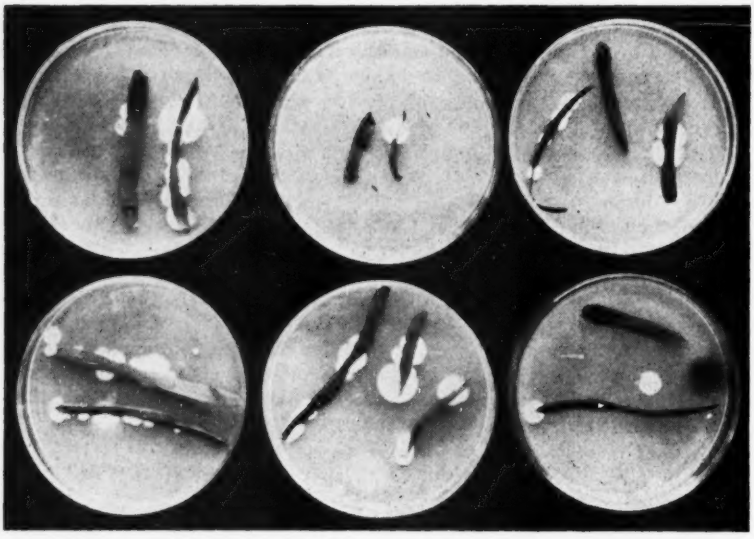


FIG. 4.—Slices cut from 8/64-inch wall of GR-S insulation after 29 months in soil. Six days on nutrient agar.

fungus "in transite" in the wall. Two samples were tested, one in which the insulation resistance had dropped 3 decades after twenty-four months of soil exposure, the other which still showed normal insulation resistance after thirty-two months The samples were washed, dried, and painted with strong iodine solution. The surface was sliced off with a knife sterilized in a flame before each cut. Slices cut aseptically from the inner regions of the wall were placed on nutrient agar in petri dishes. Figure 4 shows the growths originating from slices cut from the failed sample. No effort was made to confine the test to the

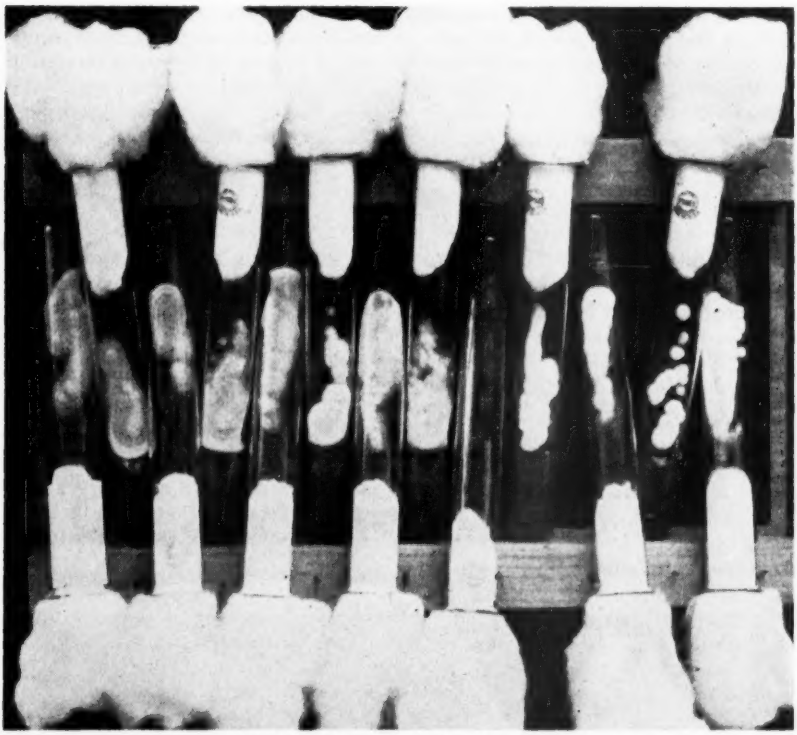


FIG. 5.—Cultures on Sabouraud's agar, each tube inoculated from a separate colony shown in Figure 4.

actual failed spot, since it was suspected that there were fungus hyphae throughout the length. Nutrient agar was used in this test in order that bacteria, if present, might develop as well as fungi. Figure 5 shows cultures inoculated from the most prominent colonies of Figure 4. Eight of the tubes showed only Spicaria violacea Abbott; four showed two other fungi which were assigned by G. T. Johnson of the University of Arkansas to the genus Stemphyliopsis and the genus Fusarium. Slices cut aseptically from the sample showing normal insulation resistance after thirty-two months in soil likewise developed fungus growth. Spicaria was again present but not so predominantly.

EFFECT OF FUNGUS FILAMENTS ON DIELECTRIC STRENGTH

Although fungus hyphae not extending completely through the wall have a negligible effect on the insulation resistance, they would be expected to lower the dielectric strength. The eight remaining samples were broken down, half with alternating voltage, half with direct voltage.

Normal dielectric strength for this insulation after thirty-two months in water would be over 500 volts per mil alternating current, 1000 volts per mil direct current. It is apparent that fungus filaments in the wall affect the dielectric strength adversely. The values of 91 and 82 volts per mil for samples showing 4.5 and 0.006 megamegohms suggest that some hyphae were nearly but not completely through the wall. Since there are doubtless service conditions where dielectric strength is more important than extremely high insulation resistance, it would be worthwhile to break down groups of replicate samples after various periods in soil to detect incipient and progressive microbiological deterioration. Tests of dissipation factor and capacitance versus exposure have not been made but might throw light on the progress of attack.

PASSAGE OF FUNGI THROUGH NEOPRENE JACKETS

The ability of Neoprene jackets to protect underlying insulation by preventing passage of fungi can be tested in several ways. Because the low inherent electrical resistivity of most jacket compounds tends to mask the drop in insulation resistance caused by fungi, the usual test of wire samples insulated with a wall of Neoprene alone would be generally unsuitable. A functional test can be made by exposing jacketed samples of vulnerable insulation to soil and measuring the overall insulation resistance. Many such tests have been made of samples with 35-mil Neoprene jackets over thin vulcanized natural rubber latex and extruded natural rubber and GR-S insulation of types having low water absorption. Both ordinary, that is vulnerable GR-S and very stable fungitoxic GR-S compounds have been tested. As controls, replicate jacketed samples were immersed in water and nonjacketed samples of the particular insulations were buried in soil.

TABLE VI

ELECTRICAL FAILURES IN NEOPRENE-JACKETED SAMPLES

Insulation	Wall (inch)	Normal 100% failure time without jacket	Failure with Neoprene jacket
NR latex	0.018	2 to 4 weeks	25% failed in 9 months
NR extruded	3/64	3 to 5 months	50% failed in 9 months
GR-S	3/64	6 to 9 months	50% failed in 38 months
GR-SY	3/64	over 48 months*	over 48 months*

* No failures, tests still going on.

No controls in any of the groups have failed in water. Typical results in the soil tests are given in Table VI.

Many Neoprene compounds exposed to soil become heavily coated with fungus. A test was made to see if stable GR-S insulation would be damaged by such growth close to it. Samples of this insulation wrapped with an open spiral of Neoprene jacket material have shown normal resistance during four years in soil. All evidence to date is that to cause failure of insulation resistance, the fungi must pass completely through the wall.

ELECTRICAL AND MICROBIOLOGICAL TESTS ON JACKETED VULNERABLE GR-S INSULATION, JACKET BLISTERS

The first sets of jacketed samples having latex and natural rubber insulation failed in eight to twelve months. Jacketed GR-S samples showed greater stability.

Particularly interesting results were obtained with samples of ordinary GR-S insulation under a 35-mil black Neoprene jacket. The controls in water showed normal resistance throughout the thirty-nine months' test. The nonjacketed wires had failed in soil in ten months. Of the ten jacketed samples in soil, one had failed after sixteen months, five after thirty-nine months.

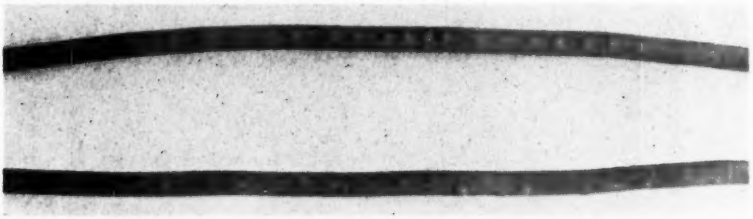


FIG. 6.—Water blisters between 35-mil Neoprene jacket and GR-S insulation after 39 months in soil.

When the ten samples were cleaned and examined, they showed water blisters between jacket and insulation over practically the whole area exposed to soil. Figure 6 shows typical sections. Since five had failed electrically, presumably because fungi had passed through both the Neoprene and the GR-S insulation, it was of interest to test all ten samples for presence of fungi in the interface between jacket and insulation. Culture tests were made in several different ways. After the jacket was surface-sterilized, it was stripped progressively from short sections, which were placed in petri dishes on nutrient agar. Figure 7 shows some of the resulting cultures. The predominant organism was Spicaria violacea Abbott. Another occasional fungus has not been

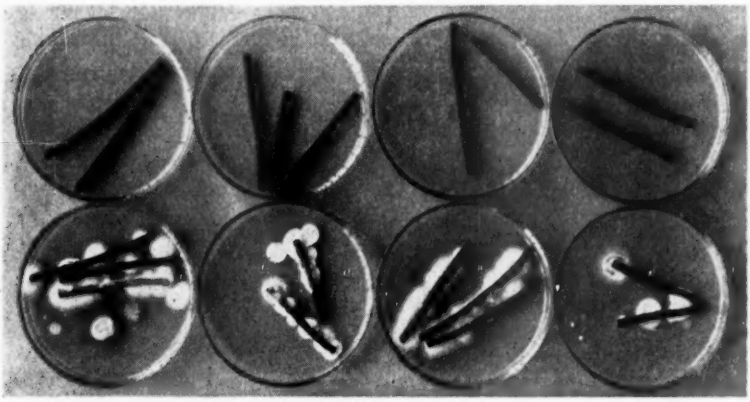


FIG. 7.—Cultures of GR-S insulation with jacket removed. Top row samples in water 39 months, no blisters or fungi. Bottom row samples in soil 39 months, blisters and fungi.

identified. Practically every inch of the ten soil test samples, and of the four water test samples, was cultured. Although only five of the samples in soil had failed electrically, all ten showed water blisters and fungus in the interface. None of the samples that had been in water thirty-nine months showed any blisters, any water between the layers, or any fungus in the culture test. If the blistering had been caused by mere diffusion of water, we should expect water blisters to be present here as well as in the soil test samples. In this experiment

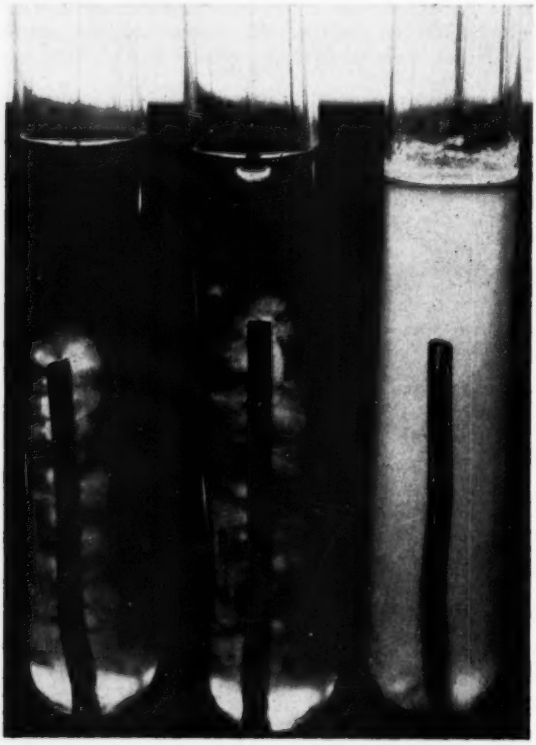


FIG. 8.—Pieces of stripped GR-S insulation from sample like that in Figure 6 after 4 days in nutrient broth. Fungus is Spicaria violacea Abbott. Cloudy tube has bacterial contamination.

the correlation between blistering and fungus passage through the jacket seems to be complete.

Figure 8 shows another way of culturing the stripped infected insulation. The interesting point is that two of the pieces show pure cultures of Spicaria violacea Abbott. If any bacteria are present, either originally or as a contamination, they may overgrow fungi as in the cloudy tube. Cases where cultures of blisters showed bacteria have been decidedly in the minority. The bacteria may have entered after the fungi and then suppressed them.

It would be difficult or even impracticable to strip and culture pieces of large cable. A very easy technique is to transfer the liquid asceptically from blister to culture plate with a sterile camel's-hair brush. Figure 9 shows such

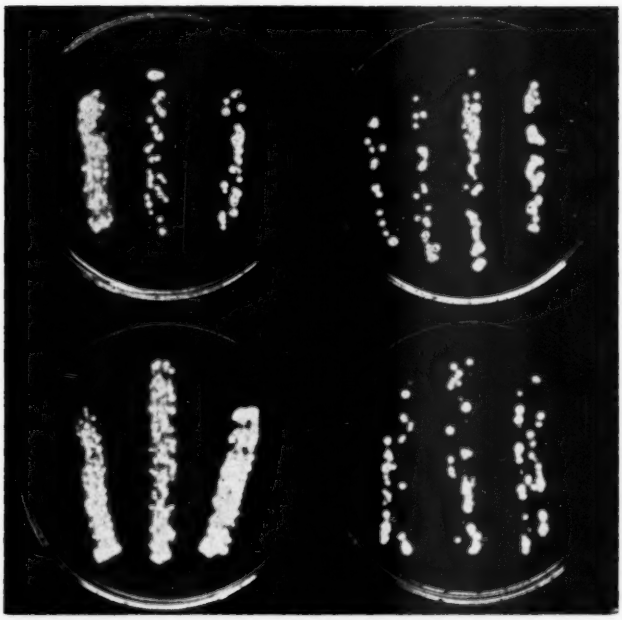


FIG. 9.—Cultures of liquid transferred by sterile brush from blistered sample like that in Figure 6. Fungus is Spicaria violacea Abbott.

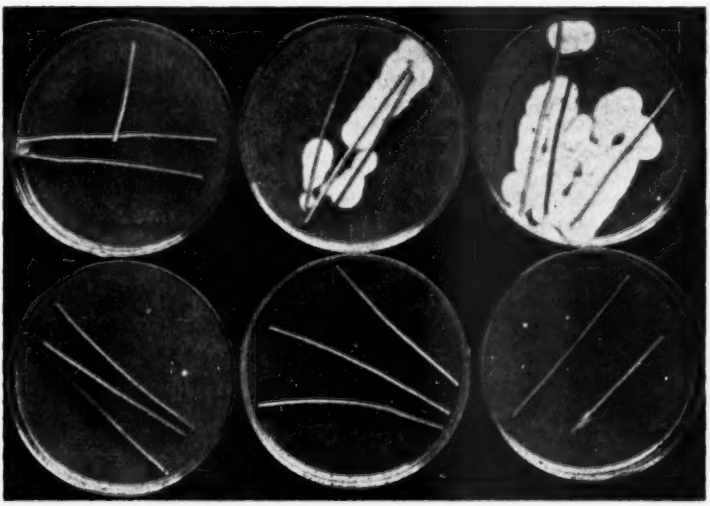


FIG. 10.—Cultures of natural rubber latex insulation with jacket removed after 2 years in soil. Fungus is Spicaria violacea Abbott.

a brush cuture from blisters in one of the preceding ten samples. The organisms proved again to be Spicaria violacea Abbott. It is also worthwhile to test the pH of the fluid. This is sometimes alkaline, suggesting some electrolytic action having nothing to do with fungi.

It would certainly be incorrect to attribute all blisters found in cables in service to microbiological attack. Some blisters when carefully tested have proved completely sterile. These laboratory results merely show that fungus attack can be one of the causes.

Figure 10 shows plate cultures of stripped latex insulation from wire having a 35-mil Neoprene jacket. Here again the organism was pure Spicaria violacea Abbott. The infection was confined to only a portion of the sample, showing that the fungus had gotten through in only one or two regions. These were from one of four groups of samples of similar construction but with different jacket compounds. In each group, eight samples were in soil, four in water. No samples had failed in water after two years. Of the thirty-two in soil, only four had failed electrically. These were all in the same group. Thus most of the jacket had so far prevented access of fungi to this insulation, which would be expected to fail within a month of the time it was reached by fungus. The greater stability of these samples compared to earlier ones of similar construction is attributed in part to better processing. In these the jacket was applied in such a way that the Neoprene stock was under compression after extrusion. The results suggest that ideal processing might make the Neoprene completely impermeable to fungi. It should be emphasized that the aforementioned experiments all involved thin walls. Thicker walls of Neoprene would be less likely to contain mechanical flaws and might be capable of preventing passage of fungus indefinitely unless mechanically damaged. Tests of a range of thicknesses are in progress, but the thickest wall on which positive results have so far been obtained is $\frac{3}{64}$-inch.

CULTURE TESTS ON AGAR-FILLED NEOPRENE TUBES

Agar-filled tubes (see Figure 1) of a number of Neoprene compounds have been in soil for several years. After 15 months in soil, two samples having $\frac{3}{64}$-inch wall of black Neoprene and two of white Neoprene containing a hard clay filler were tested by squeezing the agar onto culture plates. Both white Neoprene samples contained fungus throughout the whole exposed length of five feet. One of the black Neoprene samples showed fungus only in a short region near the middle. The other sample was sterile throughout. Apparently the fungus had entered at only one point in this sample, whereas in the white samples fungus had been able to get through practically everywhere.

A test of this type is very convincing, and is a functional one in that it shows whether fungi have actually traversed the wall. It has two disadvantages. There is no way of knowing when fungi first get through except by cutting the sample and examining the agar. If for any reason, such as failure to keep the soil damp, the agar fill dried it cannot be dissolved or swollen again unless heated to about 212° F. This happened to many Neoprene samples after long exposure. They could be saved by filling with fresh agar and connecting to a reservoir, but this would not be good routine practice.

The following is a better general method of testing jacket compounds functionally as fungus barriers. Instead of tubes of Neoprene, stranded conductors having extruded walls of Neoprene of various thicknesses are used. These are connected to a reservoir containing nutrient broth, the assembly is sterilized,

and the sample is buried in soil. Some broth is drawn off periodically and cultured. In this way it is possible to know within a few days when the first organisms have passed through the wall. These can be identified. Throughout the test, the sample itself is not disturbed. Once set up, such samples require little attention. With thick walls of Neoprene of good texture, the tests doubtless would run for some years. With proper care the results should be conclusive.

SUMMARY

Experiments on natural rubber and GR-S insulation in various forms have shown them to be inherently vulnerable to fungus attack unless made sufficiently fungitoxic. Stable fungitoxic GR-S compounds have been developed in this work which have invariably maintained normal high insulation resistance during four years in active soil.

Thin Neoprene jackets may be permeable to fungi so that underlying insulation should be fungitoxic or inherently stable.

A humid atmosphere as in a wet duct may be a dangerous environment. It has been shown that inoculated wire can fail in moist air due to fungus penetration.

Parallel electrical tests on wire and culture tests on agar-filled tubes demonstrated that the electrical failures in soil were caused by fungus penetration. It was possible to detect and identify fungus in transit in thick walls of GR-S insulation. Three types of fungi which can pass through rubber insulation and thin Neoprene jackets have been identified, at least by genus. The most prevalent has been Spicaria violacea Abbott.

The presence of fungus in insulation lowers the dielectric strength before the filaments have passed completely through the wall. Impending failure can be detected by voltage breakdown tests.

Rubber insulation in buried cables must be sufficiently fungitoxic. Great care is required in formulating stable compounds to insure that other required properties are not harmed.

REFERENCES

[1] Blake and Kitchin, *Ind. Eng. Chem.* **41**, 1633 (1949); RUBBER CHEM. & TECHNOL. **23**, 117 (1950); Blake, Kitchin, and Pratt, *Trans. Am. Inst. Elec. Engrs.* **69**, Part II, 748 (1950); RUBBER CHEM. & TECHNOL. **24**, 399 (1951).

[2] Blake, Kitchin, and Pratt, *Trans. Inst. Elec. Engrs.* **69**, Part II, 748 (1950); RUBBER CHEM. & TECHNOL. **24**, 399 (1951).

ULTRASONIC WAVE STUDY OF SWOLLEN BUNA–N RUBBER *

A. W. NOLLE

DEPARTMENT OF PHYSICS, UNIVERSITY OF TEXAS, AUSTIN, TEXAS

AND

J. F. MIFSUD

DEFENSE RESEARCH LABORATORY, UNIVERSITY OF TEXAS, AUSTIN, TEXAS

INTRODUCTION

It has been established by previous ultrasonic measurements that the longitudinal-wave ultrasound velocity in various high-polymer substances increases with decreasing temperature and that the attenuation possesses a maximum with respect to temperature. This has been verified in the case of high polymers in latex solution[1], in the case of polymer liquids of relatively low molecular weight[2], and in the case of solid rubberlike polymers[3]. Increasing frequency produces effects qualitatively similar to those produced by decreasing temperature. Also, with regard to polymer solutions in particular, work at audiofrequencies has shown that related dispersion effects exist in the oscillatory shear response of polymers in solvents of low molecular weight[4]. In particular, Ferry[5] has shown that the maximum shear modulus contributed by polymers in solution is proportional to the concentration and a similar finding has been reported[1] with reference to the ultrasonic attenuation in low-concentration latex solutions.

Now, when the concentration of a high polymer in solution becomes large, it becomes experimentally difficult to investigate the solution by the techniques which are convenient for liquid specimens so that there is difficulty in carrying experiments on solutions of high molecular-weight polymers to the limiting case in which the concentration of the solvent is negligible. It seems appropriate to extend the work on high polymers in solution to the limit of the pure polymer through a study of swollen vulcanized rubber. Vulcanized rubber allowed to come into equilibrium with suitable concentrations of an appropriate solvent will absorb enough solvent to reduce the polymer concentration to less than fifty per cent of the value associated with the pure polymer. The resulting swollen specimen, although its volume is increased, retains its initial shape and is treated experimentally by the techniques appropriate for solids. Under these conditions it is possible to carry out measurements for approximately that range of concentrations which is unsuitable for fluid-specimen techniques.

This article describes and interprets measurements of ultrasonic velocity and attenuation in swollen specimens of a Buna-N (Hycar OR-15) soft vulcanizate. The solvent is 2-butanone (commercially listed as methylethyl ketone and hereafter designated simply by MEK). The frequencies are 2, 5,

* Reprinted from the *Journal of Applied Physics*, Vol. 24, No. 1, pages 5–14, January 1953.

and 10 megacycles. It is reasonable to assume that the results for this vulcanized specimen represent essentially the behavior of the raw polymer at the specified concentrations, inasmuch as the test frequencies are above the range in which moderate cross-linking has an important effect on dynamic behavior. The vulcanization of the rubber used in these experiments is important chiefly as a means of stabilizing the dimensions of the specimen. (Another effect of cross-linking is to impose an internal pressure in the system; we are not in a position to estimate the importance of this effect, and will not consider it further.)

PROPERTIES AND TREATMENT OF THE SPECIMEN

The composition of the rubber vulcanizate is as follows, in parts by weight: Hycar OR-15, 100; zinc oxide, 5; sulfur, 1.5; benzothiazolyl disulfide, 1.3. The compound is cured under pressure for 60 minutes at 143° C in the form of flat molded sheets, the approximate thickness of which is either 0.03 or 0.08 inch.

Prior to each ultrasonic experiment, the specimen, a disk of approximately 2-cm. diameter, is allowed to swell at room temperature in a mixture of solvent and nonsolvent. The fraction of solvent in the mixture governs the degree of swelling attained at equilibrium. In the present work where the solvent is MEK, the nonsolvent is usually denatured alcohol, which has the desirable property of forming mixtures with the solvent which are sufficiently fluid and low in acoustic attenuation to meet experimental requirements at temperatures as low as −90° C. Alcohol (ethyl) is not, however, strictly a nonsolvent, but produces at a slow rate a relatively small swelling of the Buna-N compound. For this reason, water, rather than alcohol, is used as nonsolvent in the case of the lowest two of the several solvent concentrations found in this study. The significant ultrasonic effects for these lower solvent concentrations are found at sufficiently high temperatures that the reduced freezing point attainable with alcohol mixtures is unnecessary. The additive swelling due to alcohol assumes less importance at the higher MEK concentrations.

The rubber sample, when placed in the ultrasonic apparatus, is immersed in a bath having the same composition as the original swelling solution. The ultrasonic apparatus is filled with water for study of unswollen specimens; no measurable swelling has been observed with water.

For experimental simplicity the concentration of the solvent in the swelling bath is stated in terms of the volume per cent of MEK with respect to the total component volumes measured before mixing. The per cent concentrations, thus defined, are 0, 2 (both with water); 5, 15, 30, 40, 50, and 60. In each case the total volume of the swelling bath is made great enough that passage of solvent into the sample reduces the solvent concentration in the bath by no more than two per cent of the nominal value.

It is not the primary purpose of this investigation to add to the extensive literature concerning the dimensional aspects of swelling, but a limited study of the dimensional swelling aspects of the present polymer-solvent system has been carried out to ascertain how long the vulcanizate must be swollen for an acceptable approach to equilibrium, and to obtain information leading to the density of the swollen specimen. Portions of this study are summarized in Appendix I. The essential conclusions which are pertinent to the ultrasonic investigation are the following:

(1) An acceptable approach to swelling equilibrium is obtained in six hours at room temperature.

(2) The combined volume of polymer and solvent, at 25° C, decreases by less than 1.5 per cent of the initial volume of polymer when swelling occurs in pure MEK.

(3) The fractional increase in volume of the specimen, produced by equilibrium swelling in a given mixture, is substantially independent of the temperature at which swelling occurs.

(4) The rate of swelling increases with increasing temperature.

(5) The volumetric thermal expansion coefficient for the unswollen vulcanizate is 0.0012/C°, as measured in the range 0° C to 80° C. This value is closely equal to the expansion coefficient for MEK as derived from 0° C and 20° C densities[6].

(6) The relative rate of approach to swelling equilibrium (or alternatively, the apparent time constant) is not strongly dependent upon solvent concentration in the swelling bath.

(7) The diffusion coefficient for MEK swelling is of the order of 50 times that for ethyl alcohol swelling.

The term equilibrium applies only in an arbitrary fashion to the swelling process. We observe, as have previous investigators in the study of other polymer-solvent systems, that gradual dimensional changes occur at least for several days, even though it would be predicted from the apparent diffusion coefficient for initial swelling that dimensional changes should be unobservable after 24 hours. For present purposes we understand by "swelling equilibrium" a state such that further thickness change (other than that due to thermal expansion) is expected to be less than one per cent in an experimentation period of no more than four hours. Beyond this requirement of dimensional stability, and the requirement that the sample be nearly homogeneous, we are not directly concerned with swelling equilibrium, for the analysis of experimental results is referred to solvent content actually realized in the specimen, and not to solvent concentration in the swelling bath.

Since the polymer and solvent volumes are almost strictly additive in the swelling process (item 2 above), we compute the density of the swollen specimen at 20° C from the known density of the original vulcanizate at this temperature (1.05 g. per cc.), the known density of MEK at 20° C (0.805 g. per cc.), and the experimentally observed dimensional increase, the assumption of additive volumes being used in all cases. From the results of a direct measurement of volumetric changes for swelling in pure MEK (Appendix I), we find that the error in the density calculation is less than 0.5 per cent for swelling in the pure solvent; presumably the error is still smaller for the swelling achieved in the acoustic experiments. Computation of the density of a swollen specimen at temperatures other than 20° C requires use of a thermal expansion coefficient. The value 0.0012/C° is used thoughout for the volumetric coefficient, since this value is closely correct both for the solvent and for the untreated vulcanizate, and is, therefore, assumed to apply with adequate accuracy to swollen samples. No direct measurement of the thermal expansion coefficient has been made for a swollen sample.

Experimental acoustic results are affected by the detailed history of the specimen, as regards total swelling time in a given experiment. and also previous exposure to solvent. Nevertheless it appears that the acoustic results bear a unique relation to the solvent content of the swollen sample at the time of

measurement, except that, when a specimen which has previously been exposed to large solvent concentration is examined at very small swelling, the acoustic results differ from those for a previously untreated specimen. (It is possible that a portion of this discrepancy disappears over a period of several weeks; dimensional changes are noticeable for at least 30 days as a sample is allowed to deswell in air.) Because of the sensitive dependence of acoustic results on treatment of the sample, we include a complete account of procedure in Appendix II. To avoid the discrepancy noted above, we have avoided (except in one instance) performing measurements for a given degree of swelling with a sample which has previously been exposed to a larger solvent concentration.

The swelling time was in general 24 hours, except that a few initial measurements were made with three hours of treatment. Large variations in the swelling period were incurred in some cases when equipment adjustments were necessary. The maximum swelling time was 72 hours.

EXPERIMENTAL METHOD

Basically the experimental method is one previously described[7], in which the flat specimen is introduced at will into the liquid path traversed by pulsed ultrasonic signals between a single quartz crystal, which acts as source and receiver, and a plane reflector. The changes of amplitude and arrival time of the reflected signal, as a result of insertion of the sample, are observed. The apparatus is similar to that described by Nolle and Mowry[7], except that the liquid medium and the specimen are contained in a tank of modified design, having an opening only at the reflector end. This tank is almost completely immersed in alcohol in a Dewar flask. Electric stirring motors are provided for both the specimen tank and the surrounding bath. This arrangement allows satisfactory control of temperatures as low as $-100°$ C. Heating and cooling of the bath may be adjusted through control of the rate of flow of liquid nitrogen into a heat exchanger located in the bath, and through control of the power applied to an electric immersion heater.

The sample thickness is measured with a micrometer caliper (Appendix II). The velocity of sound in the liquid transmission medium is computed from the echo arrival time for the liquid alone, the effective path length required in this computation being evaluated when the tank is later filled with water at a known temperature. When the sample thickness, the sound velocity in the liquid, and the echo time delay due to the sample are all known for a particular temperature, a straightforward calculation[7] leads to the velocity of sound in the specimen at that temperature. Values of the specimen thickness, and of the decibel reduction of echo amplitude occurring when the specimen is inserted in the signal path, lead to the acoustic attenuation (in db./cm.) of the specimen at a particular temperature, when a correction is made for reflection losses at the boundaries of the specimen[8]. The reflection correction involves the ratio of the sound velocities of specimen and liquid, and the ratio of the densities. The room-temperature density ratio is used in the correction, for the thermal expansion coefficients of the specimen and the liquid are nearly equal, and high precision is not required in the reflection correction. The sound velocities are available from the preceding calculations.

Greatest accuracy in attenuation values is obtained when the specimen thickness is so chosen that the signal loss observed at the temperature of maximum attenuation has the largest conveniently measurable value. In general, we follow this criterion and obtain maximum insertion losses of 35 to 40 decibels,

although it was not feasible to obtain losses exceeding 20 decibels for the largest two solvent concentrations. Reliable attenuation measurements can be made only in that range of temperatures in which the total loss in the specimen is great enough to prevent objectionable errors arising from standing waves within its boundaries. Therefore we make no attenuation calculations where the total loss is less than 15 decibels, except that values as small as 10 decibels were tolerated at the two greatest solvent concentrations. The vulcanizate is available in two values of thickness, as already stated; further adjustment is obtained by clamping multiple layers in close contact.

In previous applications of the method, the operator has measured arrival times for the reflected signal by bringing the leading edge of the pulse envelope (displayed on a cathode-ray screen) to the beginning of a delayed oscilloscope sweep. The oscilloscope[9] is provided with a calibrated delay control, which is used in making this adjustment and from which the delay time is ready. The measurement method just described, which will be called the "envelope method", is open to two objections: (1) Theoretically the method is inexact, since the shape of the leading edge (and the trailing edge) of a pulsed signal is altered on passage through a dispersive medium such as rubber; (2) the time-difference values obtained by this method often have an experimental uncertainty as large as 0.05 to 0.1 microsecond, according to the envelope shape, whereas the delay dial graduations should allow small time differences to be estimated to 0.01 microsecond.

In order to realize more nearly the attainable precision of the equipment, we have added in the present work an additional set of time-difference measurements, obtained by the differential phase method. In this method, the operator uses the delayed sweep adjustment to determine the time shift of a particular sinusoidal maximum occurring near the middle of the pulsed signal train, where steady-state conditions are approximated. This is inherently a phase-change measurement rather than envelope or group measurement. While the time delay can be read to the precision of the equipment when the differential phase method is used, the time delay value is uncertain by integral multiples of the signal-frequency period, since the operator may unknowingly select different individual sinusoidal maxima in the wave train for the sample-in and sample-out measurements.

In the present experiments, several time-delay measurements by each method are obtained at each temperature at which a given specimen is investigated. Then for this specimen a plot is made of time delay, measured by the envelope method, as a function of temperature. A smooth curve is drawn through the points. This curve, if determined to sufficient accuracy, indicates what values must be chosen for the quantized corrections to the differential-phase-method data. The corrected values obtained by the differential phase method are used in the final computation of velocity in the specimen. That part of the uncertainty in the final sound velocity values which is due to error in the time-delay measurement is less than one per cent when the above method is followed (with a specimen 0.080 inch thick).

Temperature is read from a thermometer immersed directly in the specimen tank. The thermometers used for this purpose have been calibrated at standard freezing and boiling points. In general, the uncertainty in the specimen temperature results from changes occurring during a series of observations, and does not exceed $\pm 0.25°$ C.

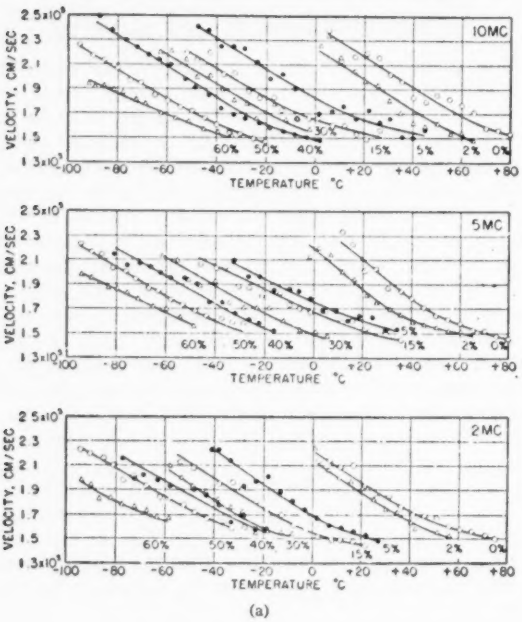
LIMITS OF ERROR IN THE RESULTS

The preceding discussion indicates that, with the best conditions attainable by the present method, random errors in sound velocity resulting from time-measurement uncertainty should be less than one per cent for a sample 0.080 inch thick. This expectation is confirmed by the narrow spread of the individual points about the velocity-temperature curves for a number of specimens of suitable thickness; moreover, in one instance an entire velocity-temperature curve (taken at 5 megacycles, with a specimen of 0.12-inch final thickness swollen in a 50 per cent solution) was repeated on a different sample, with agreement almost everywhere within one to two per cent. In general the rms. random error is of the order of two to three per cent. The additional error can be attributed in part to the effects of sudden changes of power line voltage when a regulator was not used, to slight interfacial separation in the case of multiple-layer specimens, to the use of a specimen 0.030 inch thick for the lower degrees of swelling at 10 megacycles, and to standing-wave phenomena occurring when the loss in the specimen is relatively small (the latter is in some senses a systematic error). The principal systematic error in the velocity measurements arises from uncertainty in the micrometer measurement of the thickness of the sample. This uncertainty ranges from less than one per cent, for an unswollen sample 0.080 inch thick, to three per cent for an unswollen sample 0.030 inch thick or for any highly swollen sample (the latter shrinks rapidly when exposed for measurement). Finally, it is estimated that the absolute errors associated with the smoothed velocity-temperature curves lie usually in the range of two to five per cent.

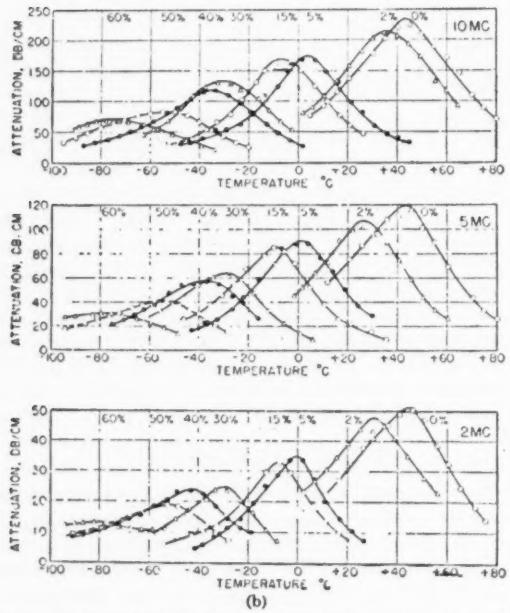
The precision of attenuation measurements depends largely on the limits within which the insertion loss due to the rubber is determined; normally the probable error is 0.4 db. (In a few cases, errors of 1.0 db were introduced by defective contacts in attenuator switches.) Since the total insertion loss ranges from 12 to 40 db, the random measurement error for attenuation, with the equipment in optimum condition, ranges approximately from one to four per cent, being least in the regions of maximum attenuation. It is estimated that the random error in final calculated values of attenuation is at most about three-halves of the variation cited above, the additional uncertainty arising in the reflection correction when there is an appreciable acoustic-impedance difference between the specimen and the liquid. Systematic attenuation errors arise through values of sample thickness, as in the case of the velocity results. Finally, with all sources of error considered, it is estimated that absolute values indicated by smoothed attenuation-temperature curves may be in error by 5 per cent at attenuation peaks and by 10 per cent at the extremes of each curve. Five per cent should be added to these tolerances for the two largest degrees of swelling, since a reduced total loss is obtained for highly swollen samples, even with maximum useable thickness.

EXPERIMENTAL RESULTS

The velocity and attenuation data derived from the acoustic measurements are shown graphically in Figure 1, in which the upper three charts contain the velocity-temperature curves for the three individual frequencies (2, 5, and 10 mc.) and the attenuation-temperature curves are similarly presented in the lower three charts. Within each chart, the various curves are identified by the "per cent concentration" of the swelling bath in which the sample was processed, according to the convention already stated. The data in Figure 1 are



(a)



(b)

FIG. 1.—Velocity (upper three charts) and attenuation (lower three charts) of ultrasonic signals in a swollen vulcanizate of Buna-N rubber, as a function of temperature. Each chart is identified according to frequency (2, 5, or 10 mc.). Numbers by individual curves indicate per cent of solvent (MEK) in swelling solution, with reference to total constituent volumes measured before mixing.

computed with reference to room-temperature values of the specimen thicknesses; the thermal expansion correction is applied, however, to data taken from Figure 1 and used in numerical calculations later in this paper. Comments on the results are enumerated below.

(1) In all cases the magnitude of the attenuation maximum is reduced, and its temperature is lowered, with increasing solvent concentration.

(2) The velocity-temperature curves shift along with the attenuation-temperature curves, with increasing solvent concentration, in such fashion that the sound velocity at the attenuation peak is roughly constant.

(3) At constant solvent concentration and constant temperature, the acoustic attenuation is roughly proportional to the frequency.

(4) A slight increase of sound velocity with increasing frequency is indicated at the lesser solvent concentrations, for temperatures above the attenuation peak, although there is reason to believe this effect is exaggerated by fortuituous combination of errors in the 10-megacycle results.

(5) For the four larger values of solvent concentration, the velocity is independent of frequency within the experimental error.

(6) The width of the attenuation peaks (the temperature interval between points of half-maximum attenuation) is not highly sensitive to solvent concentration, but first decreases with increasing solvent concentration and then increases to values somewhat in excess of the original.

(7) The width of the attenuation peaks has no significant frequency dependence.

(8) The temperature of the attenuation peak shows no systematic dependence on frequency for a specimen swollen in a bath of given concentration. (For the unswollen specimen, the temperature of maximum attenuation is constant within experimental error for the three frequencies investigated; for the swollen specimens, such variations in the temperature of maximum attenuation as are observed are not systematic and are easily explained by minor differences in the initial swelling treatment.)

The upper limit to the explored range of solvent concentration is set by disappearance of the attenuation peak into the temperature range below $-100°$ C, where no useful information can be obtained with present procedures. One investigation was performed with a sample swollen in undiluted methylethyl ketone; this specimen showed no significant insertion loss at any temperature within the operable range.

Numerical data concerning the attenuation maxima are given in Table I. These values have been corrected for thermal expansion of the specimen. Since the variations with frequency of the temperature of maximum attenuation seem to result from random differences in initial swelling treatment, the average values for the three frequencies may be taken as representative for each solvent concentration. A similar remark applies to peak widths.

In order to demonstrate the presence of irrecoverable changes in the specimen after swelling and deswelling, we examined at 5 megacycles in the unswollen condition a specimen which previously had been studied in succession at all the indicated solvent concentrations and then allowed to recover in air for more than 30 days. The temperature of maximum attenuation was 34° C, approximately 10 degrees lower than the corresponding temperature for an untreated specimen.

TABLE I

ATTENUATION–PEAK DATA

L, value in db/cm of maximum attenuation; *T*, centigrade temperature of attenuation peak; *W*, peak width in centigrade degrees; mc, frequency in megacycles/sec. See text for concentration convention.

		Per cent MEK concentration							
		0	2[a]	5	15	30	40	50	60
2 mc	*L*	50.6	47.8	35.1	33.2	25.0	24.1	19.5	13.5
	T	44.5	31.0	−0.5	−7.5	−29.5	−42.5	−52.0	−78.5
	W	50	52	34	35	39	52	58	—
5 mc	*L*	118	107	91	86	65	59	42.8	32.3
	T	43.5	26.0	1.5	−9.0	−29.0	−36.5	−54 5	−78.0
	W	51	45	42	42	46	50	55	>56
10 mc	*L*	232	212	175	170	136	120	86	74
	T	44.0	36.0	4.0	−6.5	−30.5	−35.0	−53.0	−74.5
	W	51	50	39	40	43	51	58	>58
Av.	*T*	44.0	31.0	1.7	−7.7	−29.7	−38.0	−53.2	−77.0
	W	51	50	39	40	43	51	58	>58

[a] With water as nonsolvent.

A sample swollen to near equilibrium in denatured alcohol showed maximum attenuation at 8° C (10 mc.). Thus, the effect of alcohol swelling on the loss peak at least equals the effect of the MEK absorbed from 5 per cent solution.

ANALYSIS OF RESULTS

The analysis of results will consist of (1) examination of the magnitude of the attenuation peak, and (2) examination of the concentration dependence of the temperature of maximum attenuation. The former can be done in the more satisfactory fashion. In order to establish a theoretical basis for examination of the magnitude of the attenuation peak, we present an analysis which is suggested by the work of Ferry[5].

Also basic to this analysis is a finding reported in a previous paper[10], which presents the ultrasonic properties of the present vulcanizate (unswollen) for both longitudinal and transverse waves, over a wide temperature range. In that paper it was shown (within a rather wide latitude of uncertainty) that the longitudinal-wave ultrasonic losses observed in this compound are substantially explained by shear losses. We shall assume that this is also true for swollen specimens; this assumption is reasonable at least from the point of view that the ultrasonic losses in the solvent alone are exceedingly small in comparison to the losses in the unswollen polymer.

We shall write the viscoelastic shear behavior of the specimen as the sum of the shear contributions of a group of relaxation mechanisms. (This specific notion is not necessary, but represents a convenient and commonly stated viewpoint.) The real and imaginary parts of the contribution of the ith mechanism in the unswollen polymer to the shear modulus at the temperature T_0 will be expressed by the relations:

$$u_i'(T_0) = f_i'(\tau_i\omega) \tag{1}$$

$$u_i''(T_0) = f_i''(\tau_i\omega) \tag{2}$$

where ω is radian frequency and τ_i is the relaxation time of the mechanism at

the temperature T_0. Following Ferry[5], we now introduce the following assumptions:

(1) The contribution of each relaxation mechanism is proportional to the absolute temperature (kinetic theory of rubberlike elasticity).

(2) There exists a single factor a_{TC} by which each relaxation time is multiplied when the temperature is changed from T_0 to T and when the polymer concentration is changed from the value associated with the unswollen material to the value C. It will be assumed that this is true at least for those mechanisms which contribute to the complex modulus at the attenuation peak.

(3) The contribution to the shear modulus by the mechanisms associated with any particular relaxation time is proportional to the mass of polymer per unit volume of specimen.

The mass of polymer per unit volume, referred to in assumption (3), is proportional to $[(1 + \delta_T)(1 + \delta_C)]^{-1}$, where δ_T is the thermal dilatation of the specimen associated with temperature change from T_0 to T, and δ_C is the dilatation of the specimen due to swelling. According to the assumptions, the real and imaginary parts of the shear modulus can be expressed functionally by the relations:

$$u'(T, C, \omega) = \frac{T}{T_0(1 + \delta_T)(1 + \delta_C)} \sum_i f_i'(a_{TC}\tau_i\omega) \tag{3}$$

$$u''(T, C, \omega) = \frac{T}{T_0(1 + \delta_T)(1 + \delta_C)} \sum_i f_i''(a_{TC}\tau_i\omega) \tag{4}$$

The experimental data are insufficient in general to evaluate a_{TC}, but we shall assume that the condition of a maximum of the imaginary part of the shear modulus always results from the same specific value of the summed terms in (4). This amounts to the assumption that the loss peak always represents the same relative contributions by the various relaxation mechanisms. Also, in view of our assumption that the observed ultrasonic losses arise in shear, we find from the usual equations for attenuation of ultrasonic waves the approximate relation:

$$u'' \simeq 3\rho\alpha c^3/2\omega \tag{5}$$

where α is the neperian amplitude attenuation coefficient and c is the wave velocity (both for bulk waves), and ρ is the density of the specimen.

Combination of Equations (4) and (5) gives, for the case of maximum attenuation:

$$3\rho_P\alpha_P c_P^3/2\omega = \psi T_P/[(1 + \delta_{TP})(1 + \delta_{CP})T_0] \tag{6}$$

where the subscript P indicates values associated with the attenuation peak, and ψ is the value of the sum in Equation (4) under this condition. A similar relation may be written with the subscript P_0, which refers to conditions associated with maximum attenuation in the unswollen specimen. When Equation (6) is divided by the similar relation just mentioned, and when the reference temperature T_0 is made equal to T_{P0}, the result for constant frequency is:

$$T_{P0}\rho_P\alpha_P c_P^3/T_P\rho_{P0}\alpha_{P0}c_{P0}^3, = 1/[(1 + \delta_{TP})(1 + \delta_{CP})] \tag{7}$$

This relation is readily checked by plotting of the experimental data. The method for computing density has already been explained. Data for the temperatures and heights of the attenuation peaks are shown in Table I (the

quantity α is approximately 0.115 times the attenuation in db./cm.). Velocity data are available from Figure 1. The dilatation δ_{TP} may be computed to sufficient accuracy from the thermal expansion coefficient and the average loss-peak temperatures, while the swelling dilatation δ_{CP} may be computed from the smoothed-curve swelling data of Figure 5, Appendix I.

Figure 2 shows a graphical comparison of experimental results with Equation (7). For each point, the abscissa is the experimental value of the right-hand member of Equation (7), and the ordinate is the experimental value of the left-hand member. All acoustic data have been corrected for thermal expansion of the specimen. The solid line represents the theoretical linear relationship. The sets of points derived from the three different frequencies of measurement are included in this single graph.

The fact that the experimentally determined points of Figure 2 are grouped about the predicted line may be taken as a reasonable justification for the pri-

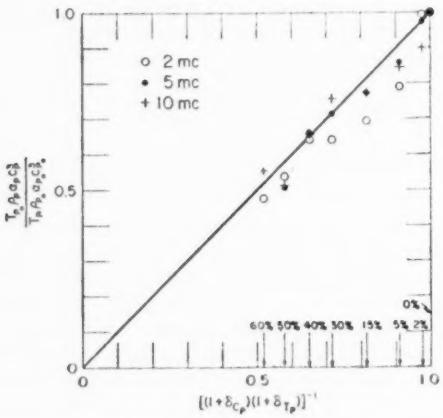


FIG. 2.—Plot of experimental values of a dimensionless attenuation parameter, derived from attenuation-peak data, against relative values of polymer mass per unit volume. The solid line indicates the relation expected on the basis that the maximum loss contribution of viscoelastic mechanisms is proportional to polymer mass per unit volume. Arrows on the abcissa identify per cent MEK concentrations in the swelling bath.

mary assumptions used in the derivation of Equation (7), which were that the maximum shear modulus is proportional to the concentration of polymer in mass per unit volume, and that the temperature dependence of all viscoelastic mechanisms contributing to the loss peak is affected in the same way by addition of solvent. The verification of Equation (7) does not either support or refute the assumption that losses arise only in shear; while this assumption is supported, for this particular compound, by other work, Equation (7) would hold in any case where both bulk and shear losses have similar dependence on concentration and temperature.

Data on relaxation processes are often interpreted in terms of an energy of activation (or a distribution of energies), under the supposition that a relation similar to the Arrhenius equation describes properly the temperature dependence of each relaxation time, or, in other words, of a_{TC} of Equations (3) and (4). If such a relation is applicable, a_{TC} is proportional to $\exp(-\Delta U/RT)$, where ΔU is an energy of activation, R is the gas constant, and T is absolute

temperature. If we take 30 kcal./mole for ΔU, an approximate value[11] from data below 100 kc. for a compound similar to the present one, we find that a_{TC} will change by a factor of two for a temperature change of about 4 C°. Since the complex modulus is a function of (ωa_{TC}), it would be expected that the temperature of maximum attenuation would increase by about 4 degrees with doubling of the frequency, in the case of the unswollen polymer. But experimentally we find, in the unswollen case, that the temperature of maximum attenuation is independent of frequency within the limit of error (Table I) and that no systematic variation is observed with swollen specimens. Either the ultrasonic behavior of the unswollen compound is governed by activation energies as large as approximately 100 kcal./mole or the relation of the Arrhenius form is inapplicable.

While the results do not allow us to calculate energies of activation, it is possible to calculate from the data the fractional change in the activation energy resulting from each solvent concentration. Even if the activation energy concept is not applicable, the analysis used for this purpose at least provides a convenient framework for relating the temperature of peak attenuation with the concentration of solvent in the specimen. We again assume that the loss peak always results from the operation of the same group of mechanisms. Accordingly, at constant frequency, the value of a_{TC} at the attenuation peak is independent of solvent concentration, or

$$\exp\ (-\Delta U_0/RT_{P0}) = \exp\ (-\Delta U/RT_P) \tag{8}$$

where subscripts 0 refer to the unswollen state. From Equation (8) we obtain:

$$-\boldsymbol{\delta}(\Delta U)/\Delta U_0 = (T_{P0} - T_P)/T_{P0} \tag{9}$$

where $\boldsymbol{\delta}(\Delta U)$ denotes $(\Delta U - \Delta U_0)$.

One explanation which has been advanced[12] for the large energy of activation for the deformation of long-molecule substances is that large segments of the molecule must progress as units over the cumulative potential barrier characteristic of a long segment. Since this requirement of coordinated motion would not be expected to apply to a group of small solvent molecules, it is reasonable to suppose that the reduction in activation energy, due to the intrusion of solvent molecules into the polymeric aggregate, is proportional to the number of solvent molecules per polymer segment, or finally to the ratio of mass of solvent to mass of polymer in a given volume of the swollen specimen. By virtue of the additive-volume property of the swelling process, this ratio is easily shown to be equal to the density of pure solvent divided by the density of unswollen polymer, the quotient to be multiplied by δ_C, the swelling dilatation. The result is independent of temperature. Numerical values for present purposes are derived by use of smoothed-curve swelling data, Figure 5, in Appendix I.

In view of the reasoning above, we plot in Figure 3 the quantity $[(T_{P0} - T_P)/T_{P0}]$ as a function of the mass ratio $(m_{\text{solv}}/m_{\text{poly}})$. The average values of T_P from Table I have been used. Note that points other than "unswollen", "2 per cent", and "alcohol only" represent combined effects of alcohol and MEK. It is noteworthy that the point for alcohol alone falls in well with the trend of the points representing combined effects. The points for samples swollen at bath concentrations greater than two per cent lie close to a single straight line as shown, but the line does not pass through the origin; hence the result is a linear relation (for high concentrations), but not the proportional relation which was suggested. In other words, an initial quantity of solvent is

required for a pretreatment or "biasing" of the specimen; for higher solvent concentrations the specimen may be regarded as a new compound which displays the expected proportional relation between $\delta(\Delta U)$, as defined by Equation (9), and solvent-polymer mass ratio. From this point of view, the swelling produced in two-per cent solution is insufficient for the initial biasing. A portion of this initial swelling effect is observable in the form of the irrecoverable change in the acoustic properties of the specimen, already described. In part the initial swelling effect certainly consists of removal of unbounded material from the specimen, for the mass is permanently reduced after a swelling and deswelling sequence (Appendix I). Presumably the material removed consists largely of polymer segments of low molecular weight and of accelerator. A further initial effect may be the releasing of local strains and entanglements which are produced in pressure molding. If this is the case, the initial effect of swelling upon acoustic properties of a specimen cast

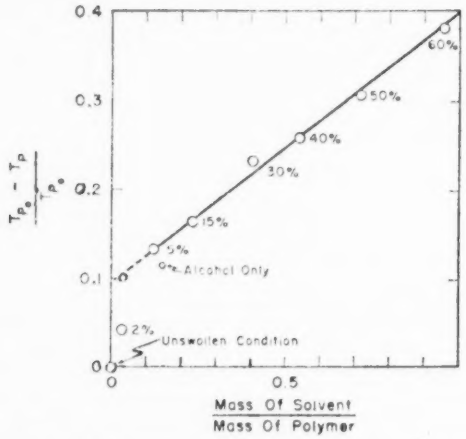


FIG. 3.—Relative lowering of the temperature of maximum attenuation, as a function of the solvent-polymer mass ratio in the swollen rubber (averaged values for 2-, 5-, and 10-mc. data). The solid line is drawn to fit the data. Numerical values beside certain points give per cent MEK in the swelling bath.

in solvent and cold-cured should differ from that observed for pressure-molded specimens. This point has not been investigated.

By extrapolating the line of Figure 3 to the value of (m_{solv}/m_{poly}), which corresponds to swelling in undiluted MEK, for which δ_C is 2.21, we find that the attenuation peak for maximum swelling should occur at $-149°$ C; from Figure 2, we estimate that the maximum attenuation should be about one-tenth the value for the case of no swelling. It is, therefore, to be expected that little attenuation will be observed above $-100°$ C when the polymer is processed with undiluted MEK, in agreement with experiment.

No quantitative conclusions concerning the bulk modulus or the real part of the shear modulus can be drawn from the temperature dependence of the sound velocity, since it is known[10] that both modulus quantities for the polymer increase with decreasing temperature. (Moreover, the bulk modulus of the solvent has a temperature dependence of the same sort.) The previous measurements for the unswollen condition[10] show, however, that for temperatures

below the attenuation maximum the real part of the shear modulus is nearly constant, so that the velocity variations in this region are due largely to variations of bulk modulus and of density. While the velocity value at the attenuation peak is approximately independent of the degree of swelling, this observation seems to have no fundamental significance and is regarded as a fortuitous interplay of the several variables involved. The sound velocity in the cases of large swelling shows no significant frequency dependence. This is to be expected, since the polymer shows no appreciable bulk-modulus dispersion[10], and in the highly diluted samples the contributions of shear modulus dispersion are too small to bring about an easily observable dispersion of the sound velocity.

CONCLUSIONS

(1) The addition of solvent to a Buna-N vulcanizate causes the temperature of maximum ultrasonic attenuation to be lowered by an amount which, in the case of large solvent concentration, is proportional to the number of solvent molecules per monomer unit.

(2) The total relaxation strength of the specimen (as measured by the peak value of ultrasonic attenuation) is proportional to the mass of polymer per unit volume, in agreement with the findings of previous investigators who have studied unvulcanized polymers in more dilute solution.

SUMMARY

The velocity and attenuation of ultrasonic waves are measured as a function of temperature in specimens of a Buna-N vulcanizate swollen to various degrees with methylethyl ketone. The frequencies are 2, 5, and 10 megacycles. The experimental method consists of determining the insertion loss and the time delay due to insertion of a flat sample in the liquid acoustic medium of a pulse-reflection apparatus; an improved technique of observation, in which phase delay as well as envelope delay is examined, leads to more precise time data than previous applications of the method. As solvent content of the specimen increases, the position of the maximum of attenuation with respect to temperature moves to lower temperatures, and the height of the attenuation peak is reduced. It is shown that the height of the attenuation peak, when corrections are made for temperature effects according to the mechanisms of rubberlike elasticity, is proportional to the mass of polymer per unit volume in the swollen specimen; moreover, the temperature of maximum attenuation is a linear function of the ratio, for the swollen specimen, of mass of solvent to mass of polymer. The latter finding indicates, if the concept of energy of activation is applicable, that the reduction of activation energy is proportional to the number of solvent molecules associated with each polymeric chain segment. The paper contains auxiliary data on dimensional and volumetric aspects of swelling and swelling rate.

ACKNOWLEDGMENTS

The authors acknowledge assistance in several forms from The Defense Research Laboratory of The University of Texas; assistance from C. J. Bronco, Jr., in the form of certain swelling-rate data; assistance from J. E. Lacy in computations; finally, the considerable help of C. S. McCleskey, Jr. (deceased) in the analysis of data.

APPENDIX I: MECHANICAL MEASUREMENTS OF SWELLING PROPERTIES OF THE VULCANIZATE

SWELLING RATE AND APPARENT DIFFUSION COEFFICIENT, MEK

Specimens of initial thickness approximately 2 mm., area 2 sq. cm., were allowed to swell in a thermostated apparatus in which a dial gauge indicated thickness directly. The specimen was located between thin metal plates in which numerous perforations allowed access of the solvent. A first series of tests yielded plots of linear strain as a function of time, for swelling in undiluted MEK at centigrade temperatures of −25°, 0°, 25°, and 50°. A second series gave similar plots, but at 50° C only, for MEK concentrations of 20, 40, 60, 80, and 100 per cent (by the convention stated previously).

If the smaller terms of higher order in the equation for diffusion into an infinite flat slab are neglected, and if the diffusion coefficient is constant, the swelling strain should be an exponential function of time. Acutally, as is well known, the diffusion coefficient in polymers is a function of solvent content, so that the observed functions are more complicated. Nevertheless, it is found that data from the latter portion of each swelling curve can be reasonably approximated by the relation:

$$S_M - S_t = S_M \exp(-t/\tau_s) \tag{10}$$

or by the equivalent relation:

$$t = \tau_s \ln [S_M/(S_M - S_t)] \tag{11}$$

where τ_s is a time constant, S_M is the apparent ultimate or maximum swelling strain, and S_t is the swelling strain at time t. The data are reduced to time constants by the following arbitrary procedure:

(1) Trial plots are made of t *vs.* the logarithmic term of Equation (11). Several estimated values of S_M are tried, since S_M is not directly observable on account of a swelling of substantially uniform rate which is superimposed in the roughly exponential portion.

(2) That value of S_M is chosen which results in a plot approximating a straight line over the greatest range of time values.

(3) The time constant is taken from the original plot of swelling strain *vs.* time as that time of which the swelling strain is 0.63 of the maximum value derived in step (2).

TABLE II

SWELLING-RATE DATA, BUNA-N VULCANIZATE IN MEK-ALCOHOL SOLUTIONS

T, centigrade temperature; τ_s, swelling time constant for 0.080-inch thickness; D, effective diffusion coefficient (see text).

T	% MEK	τ_s (min.)	D (sq. cm./sec.)
−25	100	280	2×10^{-6}
0	100	80	7
25	100	39	15
50	20	33	10
50	40	27	15
50	60	21	21
50	80	23	24
50	100	30	19

The time constant thus determined is reduced to a diffusion coefficient by the following relation, which is derived from the leading term in the solution for diffusion in an infinite flat slab:

$$D = 4l^2/\pi^2\tau_s \tag{11}$$

Here D is the diffusion coefficient and l is the slab thickness. Values of l are those corresponding to 63 per cent swelling as defined in step (3). This arbitrary procedure gives only an order-of-magnitude value for the diffusion coefficient, at an elapsed time somewhat greater than τ_s, but the relative values, particularly of τ_s, are an adequate guide in experimental procedure as noted in the body of the article. The results are given in Table II.

DESWELLING, MEK

Figure 4 shows the relative-mass *vs.* deswelling time for specimens exposed to air after 24 hours' swelling in MEK-alcohol baths of the indicated MEK concentrations. The latter stages of the deswelling process are extremely slow, and cannot be represented by an exponential time function. There is no demonstrable equilibrium at 720 hours, but the mass at this time is less than the initial mass, the decrease being 1 to 2 per cent when solutions of 60 to 100 per cent MEK concentration are used. The thickness (not plotted), which varies in similar fashion with time, decreases at least to the unswollen value and possibly to a value several tenths of one per cent smaller, for the case of initial MEK concentration of 60 per cent or greater. The combined effect, however, results in a continuous increase of density during deswelling. At 720 hours, the density is still 1 to 2 per cent below the value for no swelling.

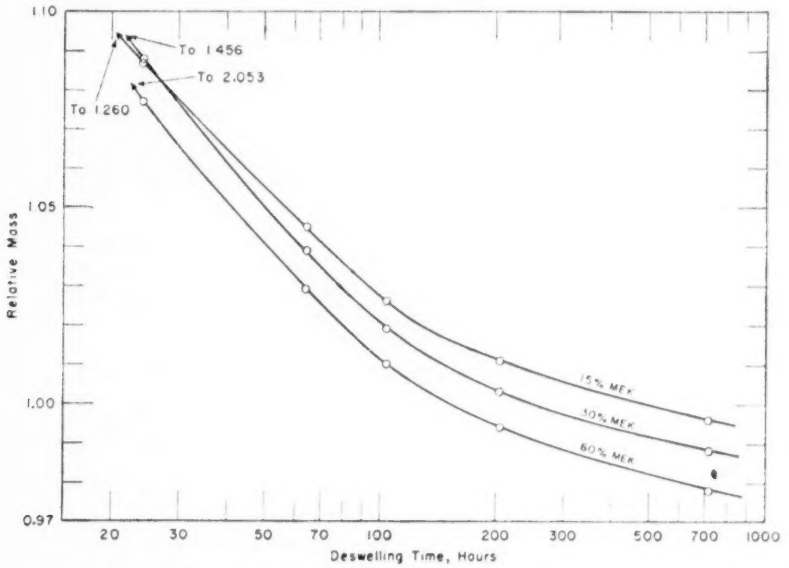


FIG. 4.—Relative mass as a function of time elapsed after removal of specimens to air from solutions of indicated MEK concentrations. Temperature 26° C. Initial swelling period, 24 hr; initial thickness, 0.080 in.; initial mass taken as unity. The 100 per cent curve (not shown) is similar to the 60 per cent curve.

SWELLING IN ALCOHOL

Swelling measurements, similar to those already described for MEK solutions, were made at approximately 26° C with ethyl alcohol, in order to evaluate the effect of alcohol as used in solution in a number of the acoustical measurements. The results can be described quite accurately by Equation (9). The diffusion coefficient is approximately 1.0×10^{-7} sq. cm./sec., with a time constant of approximately 40 hours for a sample 0.080 inch thick. The equilibrium swelling strain is approximately 0.061 with denatured alcohol (used in the acoustic work) and 0.080 with 95 per cent alcohol. This difference is unexplained. The large time constant for alcohol swelling explains some thickness irregularities in a number of specimens, used in the ultrasonic measurements, which were allowed to swell for less than 24 hours.

SWELLING STRAIN DEPENDENCE ON CONCENTRATION

Figure 5 shows the swelling strain (fractional increase in thickness) as a function of the square root of the mol fraction of solvent in the swelling bath.

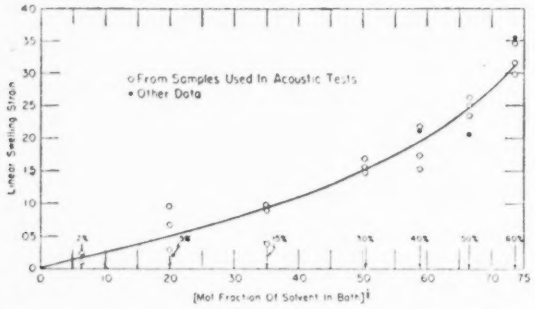


FIG. 5.—Linear swelling strain (fractional increase of thickness) as a function of the square root of the mol fraction of MEK in the swelling solution. Arrows on the abcissa indicate various concentrations according to the "per cent MEK" convention. Swelling dilatation values used for interpretation of acoustic data are derived from the smooth curve.

The values corresponding to the various per cent concentrations are indexed on the abscissa scale. The sources of the appreciable variations in swelling at each concentration have already been discussed. Values of δ_C used in the interpretation of acoustic data are taken from the smooth curve of Figure 5.

NET VOLUME CHANGE IN THE SWELLING-PROCESS

A specific gravity bottle of 20-cc. capacity was converted to a dilatometer by the addition of a long capillary tube to the stopper. A sample of the vulcanizate was allowed to swell in undiluted MEK in this apparatus, at constant temperature near 25° C. The result is that the total volume of solvent and specimen, determined by the height of fluid in the capillary, decreases by less than 1.5 per cent of the initial volume of the polymer sample in 24 hours' swelling. The result is given as a limit rather than an accurate value, as it is difficult to provide a grease seal in the ground-glass joint which absolutely prevents solvent leakage.

APPENDIX II: PROCEDURE IN TREATMENT OF THE SPECIMEN

Following initial swelling at room temperature in a bath of the desired MEK concentration, the specimen is affixed to a gatelike holder in the ultrasonic measurement tank, and the tank is filled with a portion of the swelling bath. The apparatus is then cooled to a temperature below the estimated lower temperature limit for valid ultrasonic measurements. The cooling time varies from less than one hour to two hours. Ultrasonic measurements are taken during a period of 2 to 3 hours, while the temperature is in general allowed to rise gradually; during intermittent periods when groups of readings are actually made; however, the temperature is stabilized approximately to hold the total variation during the set of readings to a total of less than 0.5 °C.

Ideally the thickness of the rubber should be measured as soon as possible after the conclusion of the acoustic measurements, but it is not permissible to disassemble the apparatus until the acoustic path length has been found from measurements with the tank water-filled. Therefore the standard procedure is to empty the tank following the swollen-sample measurements and then, after a period of at least several hours' duration for evaporation of solvent, to fill the tank with water for calibration. The sample deswells almost completely during the evaporation interval. Finally the rubber is removed and placed in a closed vessel containing a solution of the original concentration of MEK, and after a length of time equal to the original swelling period is taken out for thickness measurement. The thickness is taken as the average of ten readings with a micrometer caliper. The variability in these readings is generally less than one per cent; the important source of error appears to be rapid initial deswelling when rubber which has been swollen in concentrated solution is brought into the air for measurement. Ideally, the acoustic tank should be designed to allow thickness measurement by a method which does not require exposure of the specimen to air.

The original aim was to obtain all data for a single frequency with a single sample in a sequence of increasing concentrations. In a few cases deficiencies in the data were discovered which required repetition of measurements at certain concentrations. Fresh samples were used in these repetitions. In only one case was a sample studied at a concentration less than the largest previous value; this exception occurs in the 40-per cent determination at 5 mc., where the specimen had previously been used in 50-per cent MEK solution.

REFERENCES

[1] Cathers, Bailey, Buchy, and Asness, Abstracts of Papers Presented at the 120th Meeting of the American Chemical Society, 1951, p. 8R.
[2] Mason, Baker, McSkimin, and Heiss, *Phys. Rev.* **73**, 1074 (1948); **74**, 1873 (1949); **75**, 939 (1949).
[3] Nolle and Mowry, *J. Acoust. Soc. Am.* **20**, 432 (1948); Ivey, Mrowca, and Guth, *J. Applied Physics* **20**, 486 (1949).
[4] Philippoff, *Physik-Z.* **35**, 900 (1934); Ferry, *J. Am. Chem. Soc.* 3746 (1950); Sawyer and Ferry, *J. Am. Chem. Soc.* **72**, 5030 (1950); Ferry, Sawyer, Browning, and Groth, *J. Applied Physics* **21**, 513 (1950).
[5] Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950).
[6] Cole, *J. Chem. Physics* **9**, 251 (1941).
[7] Nolle and Mowry, *J. Acoust. Soc. Am.* **201**, 432 (1948).
[8] Nolle and Mowry, *J. Acoust. Soc. Am.* **201**, 432 (1948), Equation 6. Note that in this equation the factor "4" should read "40".
[9] The oscilloscope is the Dumont Type 256-D instrument.
[10] Nolle and Sieck, *J. Applied Physics* **23**, 888 (1952).
[11] Nolle, *J. Polymer Science* **5**, 1 (1950).
[12] Eyring and Kauzmann, *J. Am. Chem. Soc.* **62**, 3113 (1940).

CHLORINATION OF NATURAL RUBBER IN SOLUTION WITH GASEOUS CHLORINE *

C. S. Ramakrishnan, D. Raghunath, and J. B. Pande

National Chemical Laboratory of India, Poona, India

INTRODUCTION

McGavack[1], by studying the evolution of hydrogen chloride during chlorination of a rubber cement by gaseous chlorine, concluded that the first step in the reaction is wholly substitutive in character, and at later stages additive reaction of the halogen increases at the expense of substitutive attack. Bloomfield[2] examined the reaction in detail, using a solution of rubber in carbon tetrachloride. He observed that, simultaneously with the liberation of hydrogen chloride, there was a marked decrease of the iodine values of the chlorinated products, apparently indicating a considerable degree of addition of chlorine to the double bonds. The iodine value decreased to zero when the chlorine content of the product reached 58.2 per cent. In the case of simpler olefins, dihydromyrcene ($C_{10}H_{18}$) and squalene ($C_{30}H_{50}$), the amount of substitutive reaction as evidenced by the liberation of hydrogen chloride was 79 and 90 per cent, respectively. The iodine values of the final products, however, were lower than could be accounted for, if the reactions were substitutive to such an extent. Reduction of the halides gave somewhat cyclized dihydromyrcene and squalene, showing that a certain amount of cyclization did take place during the reaction of gaseous chlorine with these hydrocarbons. Monochloro substitution products of the chlorination of methyl cyclohexene also give iodine values slightly lower than the theoretical, even after allowance was made for the dichloride formed. In this case, when carbon tetrachloride was used as the solvent, the product showed a still slightly lower iodine value. The chlorination of Hevea rubber, emulsion polyisoprene and gutta-percha were re-examined recently by Kraus and Reynolds[3]. The unsaturation of the chlorinated polymers up to 30 per cent chlorine content was determined by the Kemp and Mueller method, modified by giving additional time for reaction, because of the insolubility of the chlorinated polymers and the slowness of the reaction. The unsaturation of chlorinated polymers of chlorine contents above 42 per cent were arrived at from a knowledge of the additive chlorine. According to Bloomfield the loss in iodine value observed by him in the case of dihydromyrcene is partly a real one to be attributed to cyclization, but partly an apparent one due to marked steric hindrance of iodine chloride addition to those double bonds which adjoin —CHCl— or CCl_2-groups, or which themselves form part of —CCl=C— groups. In the case of rubber also, he believes that cyclization and steric factors contribute to the reduction in unsaturation, measured by iodine value. It was decided, therefore, to study the changes in unsaturation during progress of chlorination by an independent method. The addition of ozone to unsaturated compounds and the decomposition of the ozonides formed has been widely used for determining the location of double bonds in these compounds[5].

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 4, pages 190–201, August 1953.

Recently this technique has been applied by Kharasch[6] and coworkers to arrive at a possible mechanism of dimerization of the products resulting from the attack of alkoxy radicals on chloroprene and isoprene, and also in distinguishing a double bond between two tertiary carbon atoms occurring in a cyclic

structure from a $\begin{matrix} R \\ | \\ -C=CH_2 \end{matrix}$ group.

Harries[7] and coworkers clarified the general structure of rubber by isolating levulenic aldehyde and acid as the main products of ozonization of rubber. Pummerer[8] extended the work of Harries on a quantitative basis and isolated levulenic products to the extent of 90 per cent of the theoretical.

There is not much work of a quantitative nature on the ozonization reaction. Ruzicka and Siedel[9] have used this reaction to the estimation of γ-irone, and Boer[10] *et al.*, in a study of quinolines and their homologs. Very recently, Greenwood[11] reported that the reaction between γ-octene and ozone is quantitative, and that no side reactions are in evidence.

The application of ozonization to quantitative studies has the disadvantage that the choice of solvents in which to carry out the reaction is limited. Greenwood[12] reported that ozone did not liberate halogen from carbon tetrachloride, but after passage of ozone, gave a faint color with aqueous potassium iodide. An experiment carried out by us in which ozone (6–7 per cent by volume) was passed through carbon tetrachloride for 12 hours did not reveal any development of acidity or the formation of any aldehyde. Since in our experiments we only determined —CHO and —COOH in the hydrolyzate from the ozonide, we concluded that carbon tetrachloride is a suitable solvent for this work.

The possibilities of rearrangements in allylic systems of the type R—CH=CHR′X and RCHX—CH=CHR′, when subjected to the action of ozone, have been examined by Young[13]. Their results indicate that allylic rearrangements do not take place during ozonization. Work in this laboratory[14] has shown that the absorption of ozone by rubber, as determined by the weight of the rubber ozonide obtained, cannot be used as a quantitative estimate of unsaturation, since the ozonides undergo spontaneous decomposition during drying in vacuum.

It has been found, however, that the hydrolysis of the ozonides gives acids, aldehydes, and ketones. In this investigation, the acids and aldehydes resulting from the hydrolysis of ozonides have been determined by a method[15] which excludes the determination of ketones. This is justified, since a purely ketonic compound would result on hydrolysis of an ozonide, only when a double bond occurs between two tertiary carbon atoms, of which there is very little likelihood in the possible chlorinated rubber structures; otherwise a keto-aldehyde or acid is always formed, and determination of the aldehyde or acid in such a compound is an estimate of the double bond. This applies to double bonds in cyclic structures also. Therefore, in this investigation, the determination of unsaturation in chlorinated rubber has been done by the preparation of the ozonide of the chlorinated product, hydrolyzing it, and determining the acid and aldehyde formed in the hydrolyzate. Our results indicate that there are four distinct changes in the chlorination of rubber as measured by the changes in unsaturation that accompany chlorination.

EXPERIMENTAL

1. *Rubber solution.*—3 and 4 per cent solutions of unmilled pale crepe rubber in pure carbon tetrachloride were used for this investigation.

2. *Chlorination of the rubber solution.*—The requisite amount of the rubber solution was taken in a three-necked flask fitted with a mercury seal stirrer. Chlorine gas from a cylinder, after being bubbled through sulfuric acid, was let into the rubber solution. In experiments in which nitrogen gas was used to flush out the hydrogen chloride formed, another inlet for nitrogen close to the chlorine inlet was provided. Where chlorination was carried out at a higher temperature, a water-cooled condenser was fitted to the chlorination flask.

During the progress of chlorination, samples of the solution were drawn out and dropped into excess of ethyl alcohol, and the precipitated product was immediately washed twice with further quantities of alcohol. The product was pressed out to give a thin film which was dried in vacuum.

3. *Determination of the chlorine content.*—Chlorine content of the samples were determined by the semimicro method described by Belcher and Godbert[16].

4. *Quantitative ozonization.*—About 100 mg. of dried chlorinated rubber was dispersed in about 70 cc. of pure carbon tetrachloride. Ozonized oxygen containing 6–7 per cent ozone by volume was then passed into this solution at room temperature. Ozonization was taken as complete as soon as the solution developed a bluish tinge, together with the fresh KI solution being turned red-brown by the exit gases. The solvent was then removed from the ozonide by merely passing a current of air through the solution. About 70 cc. of water was added to the syrupy ozonide. Hydrolysis of this syrupy ozonide was carried out under reflux at 83°–85° C for three hours. The flask was cooled to room temperature and the contents titrated with standard alkali, using phenolphthalein as indicator, till the pink color persisted for 30 seconds. The aldehyde present in the hydrolyzate was determined by the method of Siggia and Makey[15], in which sodium bisulfite produced by the action of a known amount of dilute sulfuric acid on sodium sulfite solution, is made to react with the aldehyde and the excess bisulfite is titrated back with standard alkali. The large excess of sodium sulfite keeps the reaction essentially complete as the excess bisulfite is titrated with alkali. The value of —CHO so determined is converted into grams of —COOH, and added to the acidity determined.

Experiments were carried out in which 100 mg. of pale crepe rubber was dissolved in 75 cc. of carbon tetrachloride, ozonized and the —CHO and —COOH in the hydrolyzate determined. The value of total acidity calculated from a given weight of rubber was expressed as per cent of the weight of the sample taken. This represents per cent —COOH obtainable when all the double bonds of rubber are intact (Table 6).

A blank experiment was carried out with 100 mg. of chlorinated rubber of different chlorine contents, refluxing them for three hours at 83°–85° C with 70 cc. of water. Any acidity developed was titrated with alkali. This value was deducted from the total value of acidity obtained from the hydrolysis of the corresponding ozonide.

RESULTS AND DISCUSSION

In the quantitative ozonization of natural rubber, the yield of acids and aldehydes obtained from the hydrolysis of the ozonide when expressed in terms of —COOH on the weight of the sample ozonized amounts to 84 per cent. In

TABLE 1

CURVE 1

Chlorination of 4% rubber solution. Chlorination carried out on 29.5.52			Solvent carbon tetrachloride. Temperature 2° C		Solution prepared on 23.4.52. Nitrogen current along with chlorine	
1	2	3	4	5	6	7
Sample no.	Chlorine content (%)	Atoms of chlorine per ($C_5H_8Cl_2$)100	Theoretical chlorine content corresponding to column 3	Hydrolysis products from corresponding ozonides expressed as %—COOH	Number of double bonds lost per 100 C_5H_8 units	Remarks
1	0.81	—	—	83.8	—	
2	6.35	15	7.1	68.6	18.3	
3	12.3	25	11.5	67.9	19.2	
4	18.1	45	18.99	49.5	41.1	
5	24.5	65	25.3	47.5	43.5	
6	27.0	70	26.7	42.1	49.9	
7	31.5	90	31.9	42.0	50.0	
8	42.2	140	42.1	37.2	55.7	
9	46.3	165	46.2	28.6	65.9	
10	49.07	185	49.07	20.47	75.6	
11	52.9	215	52.8	25.75	69.4	
12	54.7	230	54.5	20.2	75.9	
sol.	61.7	310	61.8	23.5	72.0	

other words, a value of 84 per cent —COOH corresponds to rubber with 100 per cent of its double bonds intact. In a similar manner, from the values of total acidity obtained (as explained before) from the hydrolysis of ozonides of chlorinated rubber samples, the percentage of double bonds that had not reacted during chlorination can now be easily calculated. The number of double bonds that have disappeared during chlorination would then be obtained by subtracting from 100 the value obtained for unreacted double bonds. This value is plotted along the Y-axis in the curves. From the analytical values of chlorine contents of the chlorinated products the number of chlorine atoms necessary to give the observed value of the chlorine content were calculated. This was done by calculating what the chlorine content of the product would be for the introduction of chlorine atoms one by one to 100 isoprenic

TABLE 2

CURVE 2

Chlorination of 4% rubber solution. Chlorination carried out on 16.6.52			Solvent carbon tetrachloride. Temperature 78° C		Solution prepared on 23.4.52. Nitrogen current passed along with chlorine	
1	2	3	4	5	6	7
Sample no.	Chlorine content (%)	Atoms of chlorine per ($C_5H_8Cl_2$)100	Theoretical chlorine content corresponding to column 3	Hydrolysis products from corresponding ozonides expressed as %—COOH	Number of double bonds lost per 100 C_5H_8 units	Remarks
1	9.06	20	9.43	63.2	24.8	
2	14.1	30	13.5	64.2	23.6	
3	18.5	45	18.99	54.84	34.8	
4	23.3	60	23.8	53.1	36.8	
5	38.3	120	38.4	45.6	45.7	
6	45.9	165	46.2	25.5	69.6	

units. No allowance was made for slight changes in the C_5H_4 ratio, as the maximum error would be not more than 4 per cent. These values are plotted along the X-axis. The results of the experiments are given in Tables 1 to 5 and Figures 1 and 2.

TABLE 3

CURVE 3

Chlorination of 3% rubber solution. Chlorination carried out on 24.4.52			Solvent carbon tetrachloride. Temperature 2° C		Solution prepared on 30.1.52. Nitrogen current used along with chlorine	
1	2	3	4	5	6	7
Sample no.	Chlorine content (%)	Atoms of chlorine per $(C_5H_8Cl_2)100$	Theoretical chlorine content corresponding to column 3	Hydrolysis products from corresponding ozonides expressed as %—COOH	Number of double bonds lost per 100 C_5H_8 units	Remarks
1	6.6	15	7.1	56.0	33.3	
2	14.3	35	15.4	54.4	35.2	
3	20.15	50	20.6	47.5	43.5	
4	25.5	65	25.3	46.5	44.6	
5	30.8	85	30.7	42.9	48.9	
6	33.8	100	34.1	44.7	46.8	
7	37.3	115	37.4	44.3	47.3	
8	39.05	125	39.4	32.7	61.1	

TABLE 4

CURVE 4

Chlorination of 3% rubber solution. Chlorination carried out on 12.2.52			Solvent carbon tetrachloride. Temperature 2° C		Solution prepared on 16.10.51. In the absence of N_2 stream	
1	2	3	4	5	6	7
Sample no.	Chlorine content (%)	Atoms of chlorine per $(C_5H_8Cl_2)100$	Theoretical chlorine content corresponding to column 3	Hydrolysis products obtained from corresponding ozonides expressed as %—COOH	Number of double bonds lost per 100 C_5H_8 units	Remarks
1	—	—	—	55.3	33.9	Rubber precipitated from solution before chlorination on 27.3.52
2	2.3	5	2.54	54.0	35.1	
3	2.3	5	2.54	54.3	32.8	
4	2.3	5	2.54	56.5	38.7	
5	4.4	10	4.95	51.6	36.9	
6	5.39	10	4.95	52.4	37.6	
7	10.2	20	9.43	54.3	35.7	
8	19.1	45	18.99	44.8	46.7	
9	20.5	50	20.6	44.7	46.8	
10	22.3	55	22.2	40.5	51.8	
11	27.02	70	26.7	31.3	62.7	
12	31.1	85	30.7	26.2	68.6	
13	47.3	175	47.7	26.7	68.2	
14	48.8	185	49.07	28.3	66.3	
15	49.98	195	50.4	22.6	73.1	
16	59.0	280	59.3	20.0	7.58	
17	62.3	315	61.2	13.3	84.2	

TABLE 5

SAMPLES OF CHLORINATED RUBBER REFLUXED FOR 3 HOURS AT 83°–85° C WITH WATER

Chlorine content of the sample (%)	Acidity of the water extract expressed as per cent COOH on weight of the sample
9.06	1.3
14.14	1.4
18.1	1.06
18.5	1.06
23.3	0.65
38.3	0.68
42.2	0.7
above 42	0.5

Curve 1 (Table 1), the chlorination of 4 per cent rubber solution at 2° C, with nitrogen as flushing agent for the removal of the evolved hydrogen chloride, falls into four parts or stages. In the first stage, up to the introduction of about 35 chlorine atoms per 100 isoprenic units, about one double bond is lost per atom of chlorine introduced. In the second stage, in which 105 chlorine atoms are introduced, only 20 double bonds disappear. In the third stage another 20 double bonds are lost for the introduction of 45 further chlorine atoms per 100 isoprenic units, *i.e.*, approximately 2 chlorine atoms per double bond lost. This is followed by a stage in which further introduction of chlorine atoms does not cause any appreciable diminution of double bonds.

Curve 2 (Table 2) is for the reaction carried out at 78° C, using nitrogen to flush out the hydrogen chloride evolved. The reaction is similar to the previous one, but has been only taken up to the end of the third stage. There is one difference, however, and that is, in this reaction there is an over-all decrease in the number of double bonds lost, especially in the second stage. This is attributable to the fact that under the conditions of this experiment, the possibility of the additive reaction of hydrogen chloride is less than in the previous experiment.

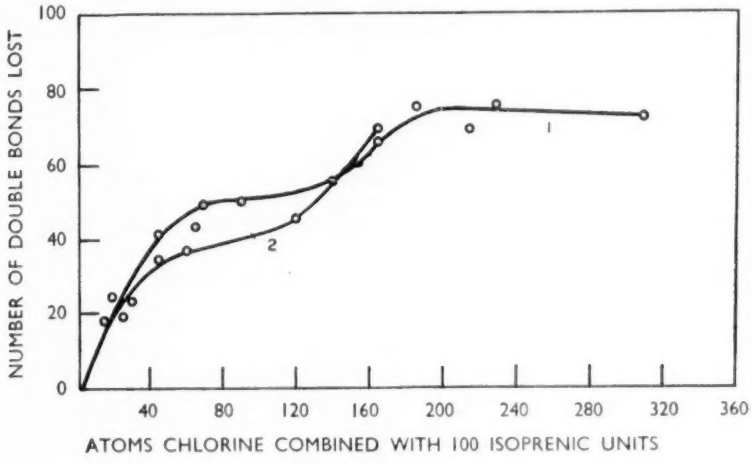


FIG. 1.

Curves 3 and 4 (Tables 3 and 4) are for experiments with rubber solutions which have been aged for some weeks before chlorination. These differ in one essential respect from curves 1 and 2. Quantitative ozonization of the unchlorinated solution just prior to chlorination shows that about 33 per cent of the original double bonds have already been lost.

In curve 3, for the reaction at 2° C, with nitrogen as the flushing agent for hydrogen chloride, for the introduction of 100 chlorine atoms there is only a loss of 13 double bonds, *i.e.*, this, more or less, corresponds to stage 2 in curves 1 and 2. On further introduction of 26 chlorine atoms per 100 isoprenic units, there is a loss of 13 double bonds, *i.e.*, approximately one double bond for 2 chlorine atoms introduced. The reactions was not carried to the last stage.

Curve 4 represents the reaction at 2° C, in which no attempt was made to remove hydrogen chloride produced by a stream of nitrogen. Here too, the first stage is missing and the second stage is represented up to the introduction

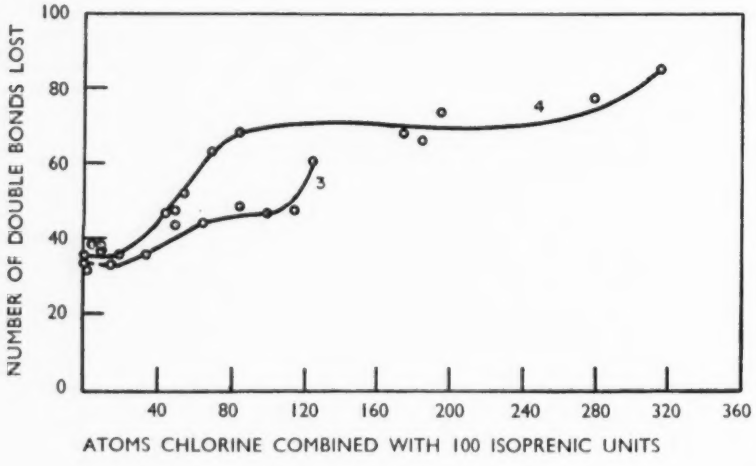


FIG. 2.

of the first 20 chlorine atoms per 100 isoprenic units. There is a marked difference from here on, for the introduction of 65 chlorine atoms per 100 isoprenic units, 33 double bonds being lost. In the earlier part of the final stage there is no loss of double bonds, but towards the end there is some loss of double bonds. This difference is attributable to the secondary reaction of hydrogen chloride evolved with the double bonds of rubber.

From his experiments on the chlorination of olefins and rubber, Bloomfield (*loc. cit.*) came to the conclusion that polyolefins are prone to cyclization, and, in rubber, cyclization appears to be complete. Kraus and Reynolds (*loc. cit.*), from viscosity determination of chlorinated polyisoprene emulsion, also came to the conclusion that cyclization does take place during the initial stages of chlorination. According to Flory[17] when adjacent functional groups are present, in a polymer chain are of such nature that they can react with one another, then on random coupling of such adjacent units, about 13.53 per cent of the original units will be left unreacted due to isolation between reacted pairs. Gordon[18] has

pointed out that cyclization of rubber is subject to this statistical effect. Accordingly, cyclization in rubber will be stochiometrically incomplete by this percentage and the unsaturation of the cyclized rubber will be 56.8 per cent of the original. This is in agreement with the figure of 57 per cent unsaturation found for cyclized rubber by Fisher and McColm[19]. In the present investigation we find that the linear relationship (stage 1) of one double bond per chlorine atom introduced into 100 isoprenic units, ceases when about 35 per cent of the double bonds have reacted, *i.e.*, when about 65 per cent of the original unsaturation remains. This experimental observation approaches the limit arrived at for the loss of double bonds by cyclization by the theoretical deductions of Gordon. Since substitutive reaction of chlorine with rubber would not lead to any loss of double bonds and additive reaction would need 2 chlorine atoms per double bond lost, stage 1 of our reaction should represent substitutive attack by chlorine, with concomitant cyclization. That chlorinated rubber is cyclized is also the view of Staudinger[20] and Le Bras and Delalande[21]. Salomon[22] investigating the infrared spectra of chlorinated rubber of different chlorine contents, observed that during chlorination the original 11.9 μ band (characteristic of RRC=CH—R) showed a weakening in the intensity in the

TABLE 6

QUANTITATIVE OZONIZATION OF PALE CREPE RUBBER

Sample no.	Weight of rubber	Acidity of hydrolyzate (g. —COOH)	Amount —CHO in the hydrolyzate	Total —COOH	% —COOH on sample at	Remarks
1	0.5078	0.3502	0.0461	0.4217	83.04	240 minutes at 100° C
2	0.5024	0.2945	0.0829	0.4228	84.1	do.
3	0.1199	0.0955	0.0033	0.1006	83.8	Hydrolyzed 3 hours at 83°–85° C
4	0.1000	0.0776	0.0035	0.0831	83.1	do.
5	0.0819	0.0610	0.0069	0.0718	87.6	do.

first phase of chlorination, with its complete disappearance when 1 atom of chlorine has been substituted. At the same time, the 11.2 μ band shifts from 11.2 to 10.6, and its intensity increases to the same order as the original 11.9 μ band. They attribute these two changes to a shift of the double bond to give a methylene group. Examining cyclized rubbers with 50, 30 and 20 per cent original unsaturation, they observed in all cases a strong band at 11.2 μ and a weak one at 11.9 μ. Therefore, the observed change in the intensities of the two bands during chlorination may as well be due to double bond shift, accompanied by cyclization. Mere shift of the double bonds cannot cause the diminution of unsaturation observed by us and previous workers referred to.

Recently, Allirot and Orsini[23], by a comparison of the position of the principal absorption bands of cyclohexane and hexachlorocyclohexane with that of chlorinated rubber of 65.5 per cent chlorine content, came to the conclusion that chlorinated rubber is cyclized and the basal unit is cyclohexanic.

Once this stage of the reaction is over, the mainly substitutive character of the reaction becomes manifest, in that, during the next stage, the loss of double bond falls much below unity per chlorine atom per 100 isoprenic units. Further, the fact that the loss of double bond does not become zero during the second stage, indicates that probably, to some extent, addition and (or) cyclization reaction is taking place during this stage. The third stage agrees with the re-

quirements of an additive reaction. Amerongen[24] *et al.*, from the amount of hydrogen chloride liberated by the reaction between chlorine dissolved in carbon tetrachloride and carbon tetrachloride solutions of rubber, came to the conclusion that below 30 per cent chlorine content the reaction is entirely substitutive and that addition of chlorine to the double bond follows the substitution of 1 chlorine atom per isoprenic unit. This corresponds to stage 3 in our curve. Such additive reactions will also explain the enhanced rate of decrease of iodine value after the initial phase during chlorination observed by Bloomfield. This stage is followed by one in which once again only substitutive attack by chlorine continues.

Mechanisms for cyclization reactions have been suggested by Bloomfield and by Farmer[25]. It may be possible also that hydrogen chloride produced by the substitutive attack of chlorine on rubber may be acting as catalyst for the cyclization reaction. It is known that usually acidic reagents are used to bring about cyclization of solid rubber as well as latex, and that the activity is dependent on the Hammett's acidity factor, as pointed out by Gordon[26].

The initial lessened unsaturation of an aged rubber solution shows that rubber has either undergone structural changes or loss of unsaturation by oxidation—oxidative degradation having exceeded any cross-linking that might have occurred in a phenomenon akin to photogelation. There has been no detailed study of loss of unsaturation during photogelation, although it is reported that there is a decrease of 2–6 per cent in unsaturation during photogelation. Our results, however, indicate a much larger loss of unsaturation.

Work is in progress in the laboratory to determine the nature and extent of the loss of unsaturation during storage of rubber solutions.

The greater loss in unsaturation observed in curve 4 during all stages indicates that addition of the hydrogen chloride takes place side by side with chlorine, if it is not removed from the system by flushing with an inert gas or its reaction with rubber reduced by carrying out the reactions at a higher temperature.

CONCLUSIONS

1. The reaction of chlorine gas with rubber is predominantly substitutive.
2. The reaction of chlorine gas with rubber solutions takes place in four stages when carried to completion.
3. The four stages can be explained as below:
   (*a*) During stage 1 substitutive attack is accompanied by a cyclization between adjacent isoprenic units, resulting in a loss of 1 double bond between 2 isoprenic units.
   (*b*) In stage 2 the predominantly substitutive character becomes evident, since cyclization is by now fairly complete.
   (*c*) In stage 3, addition of chlorine to double bonds takes place.
   (*d*) In stage 4 only pure substitution of chlorine takes place.
4. Aged solutions do not show the cyclization stage.
5. The additive reaction of hydrogen chloride produced by the action of chlorine on rubber is minimized either by carrying out the reaction at the boiling point of the solvent and(or) by flushing away with an inert gas, such as nitrogen.

SUMMARY

The chlorination of rubber solutions by gaseous chlorine was followed by isolating the partially chlorinated products and preparing their ozonides. The

ozonides were hydrolyzed, and the acids and aldehydes formed on hydrolysis were determined. By a comparison with the amounts of acids and aldehydes obtained from ozonides of unreacted rubber, the amount of residual isoprenic double bonds present was found. The loss of double bonds attending the introduction of chlorine atoms into the molecule of rubber indicates four definite stages in chlorination: (1) initial substitutive attack by chlorine, with concomitant cyclization, resulting in a loss of one double bond between two isoprenic units, (2) substitution, (3) additive reaction, and (4) essentially substitution. Chlorination of aged rubber solutions differs from the above in that the cyclization reaction (stage 1) seems to be absent.

ACKNOWLEDGMENT

The authors wish to express their thanks to the Director, National Chemical Laboratory, for permission to publish the paper, and to S. L. Kapur for valuable criticism.

REFERENCES

[1] McGavack, *Ind. Eng. Chem.* **15**, 961 (1923).
[2] Bloomfield, *J. Chem. Soc.* **1943**, p. 289; **1944**, p. 114.
[3] Kraus and Reynolds, *J. Am. Chem. Soc.* **72**, 12, 5621 (1950).
[4] Kemp and Mueller, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934).
[5] Long, *Chem. Revs.* **27**, 437 (1940).
[6] Kharasch and Acheson, *J. Org. Chem.* **16**, 447 (1951); Kharasch, Arimoto, and Nudenburg, *J. Org. Chem.* **16**, 1556 (1951).
[7] Harries and Memmler, "The Science of Rubber", Reinhold Publishing Corp., New York, **1935**, p. 214.
[8] Pummerer, Ebermayer, and Gerlach, *Ber.* **64**, 804, 809 (1931).
[9] Ruzicka and Siedel, *Helv. Chim. Acta* **31**, 257 (1948).
[10] Boer *et al.*, *Rec. trav. chim.* **70**, 6, 509 (1951).
[11] Greenwood and Wolkowitch, *J. Org. Chem.* **17**, 1557 (1951).
[12] Greenwood, *J. Org. Chem.* **10**, 414 (1945).
[13] Young *et al.*, *J. Am. Chem. Soc.* **68**, 293 (1946).
[14] Ramakrishnan, *J. Sci. Ind. Research* (India) **11B**, 6, 245 (1952).
[15] Siggia and Makey, "Quantitative Analysis via Functional Groups", John Wiley & Sons, New York, **1949**, p. 13.
[16] Belcher and Godbert, "Semimicroquantitative Organic Analysis", Longmans Green & Co., London, **1945**, p. 101.
[17] Flory, *J. Am. Chem. Soc.* **61**, 1518 (1939).
[18] Gordon, *Ind. Eng. Chem.* **43**, 386 (1951).
[19] Fisher and McColm, *Ind. Eng. Chem.* **19**, 1325, 1328 (1927).
[20] Staudinger and Staudinger, *J. prakt. Chem.* **162**, 148 (1943); Rubber Chem. & Technol. **17**, 15 (1944).
[21] Le Bras and Delalande, "Les Dérivés Chimiques du Caoutchouc Naturel", Dunod, Paris, **1950**, p. 39.
[22] Salomon, van der Schee, Ketelaar, and van Eyk, *Discussions Faraday Soc.* **9**, 291 (1950).
[23] Allirot and Orsini, *Rev. gén. caoutchouc* **31**, 1, 42 (1953).
[24] Van Amerongen *et al.*, *J. Polymer Sci.* **6**, 639 (1950).
[25] Farmer, "Advances in Colloid Science", Interscience Publishers, Inc., New York, **1946**, Vol. 2, p. 304.
[26] Gordon, *Proc. Roy. Soc.* (London) Series A, **204**, 569 (1951).

CARBON BLACK PARTICLE SIZE *

C. H. LEIGH-DUGMORE

RESEARCH CENTER, DUNLOP RUBBER CO. LTD., FORT DUNLOP, ERDINGTON, BIRMINGHAM, ENGLAND

INTRODUCTION

The electron microscope was first used to measure carbon black particle diameters in 1940 when E. F. Burton and his colleagues, using the instrument they had constructed at the University of Toronto, produced electron images of the particles of Standard Micronex-MPC black. Measurement of these images showed this black to consist of approximately spherical particles, with a mean diameter about 28 mμ and a specific surface about 100 sq. m. per g.[1] This can now be regarded as a classical experiment which provided the impetus for similar studies to be made of the different types and brands of carbon black used in the rubber, paint, and ink industries. The influence of particle diameter and specific surface on the properties of black-loaded stocks has been described by Parkinson in both natural rubber[2] and GR-S[3].

In all quantitative studies of particle size, carbon black particles have been assumed to be spherical. Although this is not strictly true, the assumption is not a dangerous one where the more common varieties are concerned; here it has been demonstrated that particles are often spheroidal rather than spherical, but the eccentricity of their images is usually so small that it can be ignored. In special types of black which are less frequently encountered, and to some extent in acetylene blacks, a higher degree of crystallinity sometimes occurs; this may cause flat surfaces on the particles and, in extreme cases, particles may be almost hexagonal. In this paper only those blacks are considered which may safely be regarded as spherical.

Specific surface has been estimated, using also the low-temperature nitrogen adsorption method of Brunauer, Emmett, and Teller[4]. Such estimates for furnace blacks usually agree sufficiently closely with results of electron microscope studies, but the two methods differ for channel blacks, the differences being more marked the finer the particle size. Dannenberg and Collyer[5] have argued that the differences between these surface estimates are due to "surface roughness and porosity" which is negligible among furnace blacks but increases with extent of surface among channel blacks.

THE DISTRIBUTION OF PARTICLE SIZE

Since the original study of Micronex-MPC black[1], it has been found that the distribution of particle diameters of any type of black is markedly skew. From a study of published diameter distributions[6] and particle size measurements made by the author, he has concluded that most, if not all, such distributions are log-normal: that is to say, the distribution of the logarithms of particle diameters is not skew but is normal or Gaussian.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 2, pages 92–99, April 1953.

This was discovered and can best be demonstrated by plotting, as in Figure 1, the cumulative frequency-distribution of particle diameters of any black on logarithmic probability paper. The scales on this paper are so arranged that particle diameter is plotted on a logarithmic scale as ordinate and relative cumulative frequency (usually as percentage) as abscissa on a scale which is proportional to the value in a normal population which divides that population so that the same percentage is of smaller size. Only if particle diameters are approximately log-normally distributed will a straight line be obtained. From this line estimates of the mean and standard deviation of the logarithmic distribution can be easily obtained (See Appendix).

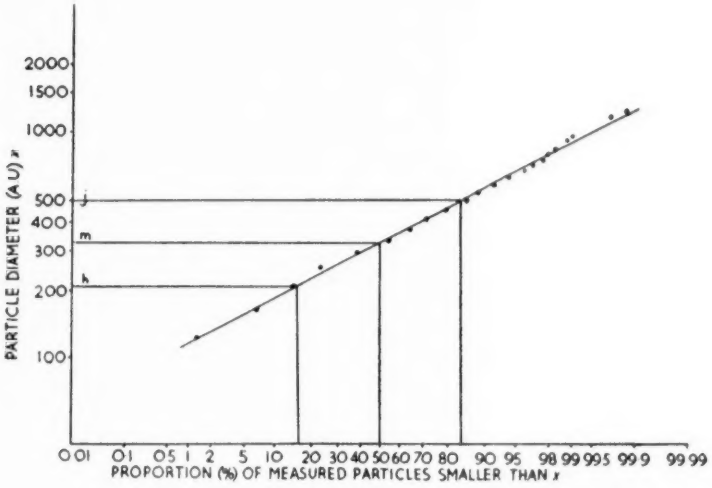


FIG. 1.—Data for Black G (Table 1) on logarithmic probability paper.

CALCULATION OF PARTICLE-SIZE STATISTICS

It has been customary to calculate the mean particle diameter, the standard deviation of the diameter distribution, and the specific surface directly from the sample frequency distribution which is the result of electron image measurements. This necessitates the summation of all the observed diameter values, their squares and their cubes. Although the labor involved is reduced when a desk calculating machine is available, it is still considerable.

It is shown in the Appendix that mean diameter, specific surface and, in fact, any function of the moments of the particle-diameter distribution are simple exponential functions of the mean and variance of the normal distribution of the logarithms of diameters. This allows an appreciable reduction of the effort spent on computation which can be achieved in either of two ways: one, by estimating the mean and variance of the log-distribution from the sums of the logarithms and their squares; the other, an even greater reduction, by plotting the cumulative frequency distribution of observed particle diameters on logarithmic probability paper and reading off the mean and standard deviation of the log-distribution (see Figure 1, which shows the data for Black G of Table 1, and the Appendix). Although it is easier and quicker than the first

TABLE 1

ESTIMATES OF MEAN PARTICLE DIAMETER AND SPECIFIC SURFACE CALCULATED FROM ELECTRON MICROSCOPE MEASUREMENTS

Black	Type	Mean diameter (A.U.)			Specific surface (sq. m. per g.)		
		Usual method	From logs	Probability paper	Usual method	From logs	Probability paper
Standard Micronex	MPC	268	269	268	95	90	92
Vulcan-3	HAF	259	261	261	90	77	73
		272	273	278	90	82	86
		289	290	289	92	84	86
Philblack-O	HAF	295	296	301	82	76	76
		312	313	302	87	79	83
Sterling-L	HMF	515	517	516	45	41	40
Experimental blacks							
A		214	216	215	108	93	95
B		295	297	299	86	79	75
C		304	304	305	76	73	73
D		308	308	308	71	69	66
E		325	326	325	78	72	74
F		342	345	339	68	62	62
G		375	373	372	59	62	58
H		396	396	394	61	58	61

and confirms, at the same time, the assumption of normality the second method is less precise (see Equations (7) to (10) in the Appendix).

Table 1 shows values of mean particle diameter and specific surface that have been calculated by all three methods, and Table 2 the range of variation among estimates of these properties that can be found in the literature. The agreement in Table 1 is considered good and comparison with the variation

TABLE 2

VARIATION AMONG PUBLISHED ESTIMATES OF MEAN DIAMETER AND SPECIFIC SURFACE

Black	Type	Mean diameter (A.)	Specific surface (sq. m. per g.)	
			Electron microscope estimate	Nitrogen adsorption estimate
Spheron-6	MPC	250–270	106–109	108–120
Vulcan-3	HAF	265–320		86–117
Philblack-O	HAF	290–330		75–77
Spheron-9	EPC	290–330	77–94	99–120
Kosmos-60	FF	272–350		70–90
Statex-K	FF			55–75
Statex-A	CF		46–71	
Statex-B	FF		39–71	
Shawinigan	—	396–430	42–65	59–65

shown in Table 2, which is perhaps much greater than many have realized, suggests that the quicker of the new methods described here, using probability paper, though in theory less precise, is sufficiently accurate for most if not all purposes.

DIFFERENCES BETWEEN SURFACE AREA ESTIMATES

Estimates of surface area obtained from electron-microscope measurements of particle diameter and from the low-temperature nitrogen isotherm method[4] do not always agree. They give similar surface estimates for blacks made by

the furnace process, most of which have mean particle diameters greater than 300 A and specific surfaces less than 100 sq. m. per g.[7] Channel blacks, whose mean diameters are usually less than 300 A and specific surfaces greater than 100 sq. m. per g., lead to different surface estimates by the two methods; the adsorption estimate is the greater and the difference between the two increases with the extent of the surface. Dannenberg and Collyer[5] have explained this by attributing to the fine impingement blacks a porosity or unevenness of particle surface on a scale too fine to be resolved by the electron microscope, yet coarse enough to be open to the nitrogen molecule.

A colleague of his, B. J. A. Martin, and the author at one time thought that this difference might more likely be due to lack of resolution by the electron microscope of the finest particles. The coarsest channel blacks have particles whose diameters range in size from something less than 100 A to about 500 A. Since many electron microscopes have resolution limits, in practice, of about 50 A, it seemed reasonable to imagine that, as specific surface increased and mean particle diameter decreased among the finer channel blacks, there might be present more and more particles whose diameters were smaller than the limit of resolution. These would not be imaged and so would be omitted from

TABLE 3

Black	Type	Mean diameter (A.U.)	Specific surface (sq. m. per g.)		
			Electron microscope estimate	Adsorption estimate	Expected highest
Carbolac-1	—	100	264	1,000	440
Spheron-N	CC	176	145	419	185
Spheron-C	CC	231	110	227	160
Spheron-1	CC	230	114	188	155
Spheron-4	HPC	240	105	142	155
Spheron-6	MPC	250	106	120	160
Kosmobile-77	EPC	310	87	108	125

the observed particle-size frequency-distribution. Their omission, since smaller particles contribute more surface area in proportion to their weight, would tend to make estimates of specific surface lower than they should be.

Since particle-diameter distributions appear to be log-normal, it is possible to calculate, from the size of the largest particle observed, an upper limit (Appendix, Inequality (14)) for the specific surface, which is the highest specific surface that would be expected of a black consisting only of smooth spherical particles if particles of all sizes are taken into account. Table 3 gives specific surface estimates for each of a number of blacks obtained by both methods of measurement, together with this expected highest value. These are from data published by Godfrey L. Cabot, Inc.[6], which give full results of both methods of measurement and include particle-diameter histograms.

The expected highest value of specific surface is in all cases greater than the estimate from electron microscope measurements and, where the adsorption estimate is very much larger than that from the electron microscope, it lies between the two.

Where, as with Spheron-4, Spheron-6 and Kosmobile-77 (Table 3), the expected highest value is greater than either of the estimates it could be supposed that the difference between the two estimates is due to irresolution of the smaller particles. For Carbolac-1, Spheron-N, Spheron-C and Spheron-1, the expected highest value, though greater than the electron microscope estimate,

is less than the adsorption estimate; the differences between the two estimates cannot here be wholly explained by irresolution and part, at least, must be attributed to other causes. Dannenberg and Collyer's explanation[5] remains more likely: these fine blacks have porous uneven surfaces which are not distinguished by the electron microscope. To this must be added the rider that electron microscope estimates, particularly of channel blacks, tend to be a little too low because all the finest particles may not have been resolved.

DESCRIPTION OF PARTICLE SIZE

Since any normal distribution is completely specified by two parameters, the mean and variance, if the diameters of carbon black particles are distributed log-normally, any two characteristics which can be expressed as independent linear transformations of the mean and variance of the log-normal distribution will themselves completely specify the distribution of size and, consequently, the effect of size on the properties of black-loaded stocks. A third size-characteristic, were one introduced, would be superfluous, since it could be completely defined in terms of the other two.

Mean particle diameter and specific surface fulfill these requirements as, indeed, do the mean and variance of the log-normal distribution, though the first two have more useful physical definitions. These two size properties are together sufficient, and it would be pointless to seek other quantities to express size unless they were to replace these and were more convenient to use or more easy to understand.

SUMMARY

Carbon black particle diameters tend to be distributed log-normally. This discovery has led, first, to simplified methods for the calculation of mean diameter and specific surface from electron microscope measurements; second, to a demonstration that the observed differences between estimates of surface area from electron-microscope measurements and from low-temperature nitrogen adsorption measurements cannot be entirely explained by supposing the finest particles not to be resolved by the electron microscope, thus adding further support to the porosity explanation; and third, to the argument that any two size characteristics, such as mean particle diameter and specific surface, are entirely sufficient to describe particle size and its distribution and, consequently, their influence on vulcanizate properties.

ACKNOWLEDGMENT

The author is indebted to D. Parkinson for his suggestions and for criticizing the manuscript, to L. J. Kibler for much of the work with the electron microscope and some of the particle image measurement and to (Miss) M. Davies for the computation. Acknowledgment is made to the Directors of the Dunlop Rubber Company Limited for permission to publish the paper.

APPENDIX

MATHEMATICAL NOTES

If particle diameters, x, be log-normally distributed their logarithms, y, to base 10 are normally distributed with, say, mean, $\bar{y}$, and standard deviation, σ.

Then the mean or expected value, $E(x^r)$, of the r-th powers of the diameters is given by the moment generating function of the normal y-distribution:

$$E(x^r) = \exp(ru\bar{y} + \tfrac{1}{2}r^2u^2\sigma^2) \tag{1}$$

where $u = \log_e 10 = 2.3026$

Thus the mean diameter:

$$\bar{x} = E(x) = \exp(u\bar{y} + \tfrac{1}{2}u^2\sigma^2) \tag{2}$$

and the specific surface:

$$\begin{aligned} a &= kE(x^2)/E(x^3) \\ &= k \exp(-u\bar{y} - \tfrac{5}{2}u^2\sigma^2) \end{aligned} \tag{3}$$

where, if x is measured in Angstrom units, specific surface in sq. m. per g. and the density of carbon is taken as 1.86

$$k = \frac{60{,}000}{1.86} \tag{4}$$

If log-probability paper is used to estimate $\bar{y}$ and σ, h, m, j the 15.87 per cent, 50 per cent, 84.13 per cent points, respectively, will be read off such that:

$$\begin{aligned} \bar{y} &= \log m \\ 2\sigma &= \log j - \log h = \log j/h \end{aligned}$$

(All logarithms are to base 10).
So, for purposes of calculation:

$$\log \bar{x} = \log m + \tfrac{1}{8}u(\log j/h)^2 \tag{5}$$

$$\log a = \log k - \log m - \tfrac{5}{8}u(\log j/h)^2 \tag{6}$$

The sampling variances of these estimates are given by:

$$V_1(\log \bar{x}) = \frac{\sigma^2}{n}(1.57 + 0.93u^2\sigma^2) \tag{7}$$

$$V_1(\log a) = \frac{\sigma^2}{n}(1.57 + 23.1u^2\sigma^2) \tag{8}$$

where n = number of particles measured.

If, on the other hand, $\bar{y}$, σ^2 are estimated from the sums of y and y^2 for the individual particles these sampling variances become:

$$V_2(\log \bar{x}) = \frac{\sigma^2}{n}(1 + \tfrac{1}{2}u^2\sigma^2) \tag{9}$$

$$V_2(\log a) = \frac{\sigma^2}{n}(1 + \tfrac{25}{2}u^2\sigma^2) \tag{10}$$

and are smaller because $\bar{y}$, σ^2 are estimated from moments instead of quantiles.

Now if L is the logarithm of the largest particle observed in a sample of n particles we can write:

$$L = \bar{y} + \theta\sigma \tag{11}$$

while from Equation (3):

$$\lambda = \log a = \log k - \bar{y} - \tfrac{5}{2}u\sigma^2 \tag{12}$$

Eliminating $\bar{y}$ from Equations (11) and (12):

$$\tfrac{5}{2}u\sigma^2 - \theta\sigma + L + \lambda - \log k = 0 \tag{13}$$

and since σ must be real:

$$\theta^2 \leqslant 10u\,(L + \lambda - \log k)$$

so

$$\lambda \geqslant \frac{\theta^2}{10u} + \log k - L \tag{14}$$

If a value is assumed for θ, this inequality gives an upper limit for the specific surface, which depends only on the size of the largest particle observed. θ is the extreme value of the variate in a sample from a normal distribution of mean zero and unit standard deviation and the distribution of θ in samples of different size has been studied by Tippett[8]. In calculating the expected highest values in Table 3, the expected or mean value[9] of θ has been used, since we are not using the inequality (14) as a probability limit or confidence limit in single separate cases, but are testing how far it applies as a mathematical limit to a number of cases jointly.

REFERENCES

[1] Columbian Carbon Co., Columbian Colloidal Carbons, Vol. 2 (1940). "The particle size and shape of Colloidal Carbon as revealed by the electron microscope".
[2] Parkinson, *Trans. Inst. Rubber Ind.* **19**, 131 (1943); **24**, 267 (1949).
[3] Parkinson, *Trans. Inst. Rubber Ind.* **21**, 7 (1945).
[4] Brunauer, Emmett, and Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).
[5] Dannenberg and Collyer, *Ind. Eng. Chem.* **41**, 1607 (1949).
[6] Godfrey L. Cabot, Inc., "Cabot carbon blacks under the electron microscope", **1949**; Martin and Smith, "Particle size and surface area data on a number of carbon blacks", Godfrey L. Cabot, Inc., Boston, **1949**.
[7] Since this paper was written, some manufacturers have developed superabrasion furnace blacks (SAF) with even smaller particle size and greater surface. Insufficient work has been done with these new types to show whether the two estimates agree or not.
[8] Tippett, *Biometrika* **17**, 364 (1925).
[9] "Tables for Statisticians and Biometricians", edited by Karl Pearson, Biometrika Office, Univ. College, London, Part 2.

ACCELERATOR COMPOUNDING. HEAT HISTORY AND COMPOUNDING *

B. S. Garvey, Jr., D. W. Yochum, and C. A. Morschauser

Sharples Chemicals, Inc., Wayne, Pennsylvania

In this paper we shall discuss certain phases of accelerator compounding which are related to scorch time and cure time. First, we shall illustrate certain concepts. Second, we shall show why we think they are true. Third, we shall point out some consequences of them. We shall also include a couple of slightly extraneous observations because they are interesting and because they have practical value.

Among the most important characteristics of accelerators are *scorch time*, *cure time*, and *vulcanization time*. These are illustrated in Figure 1. Both

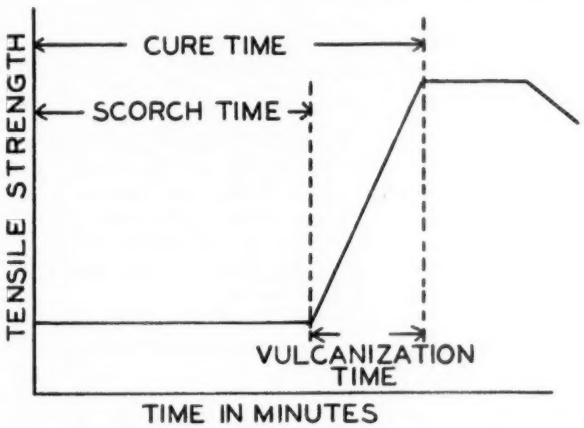


Fig. 1.—Visualization of scorch time, cure time, and vulcanization time.

scorch time and cure time are used in their usual widely accepted sense. The scorch time is the time available at a given temperature before the stock begins to vulcanize. Maximum scorch time is the scorch time at zero heat history; residual scorch time is the scorch time remaining in a specific batch at a specific time, and cure time is the time a stock must be heated in a press at a given temperature until it reaches a technically correct cure. Vulcanization time is the term we have chosen to designate the time required after vulcanization has started until a satisfactory technical cure is reached. As indicated in Figure 1, it is numerically equal to the cure time minus the scorch time.

For a given compound, both maximum scorch time (at zero heat history) and vulcanization time are characteristic constants. They depend primarily

* Reprinted from *The Rubber Age* (N. Y.), Vol. 73, No. 3, pages 361–368, June 1953.

on the accelerator, but are affected also by the sulfur ratio, pigments, softeners, and some other materials.

The maximum scorch time, however, is used up during factory processing before the product is cured. The amount of scorch time used up is equivalent to the heat history of the particular batch of compound being used. Thus, the residual scorch times for different batches of the same compound may vary widely, depending on their heat history. Although the maximum scorch time may have been 30 minutes, the residual scorch time of a particular batch may be only 20 or 10 minutes.

The vulcanization time, on the other hand, remains essentially constant regardless of the heat history of the particular batch. No matter how much of the maximum scorch time is used up, the vulcanization time remains the same. It is obvious that if the vulcanization time remains constant and the scorch time varies with heat history, the cure time also must vary with heat history.

Experimentally we shall show why we believe that the vulcanization time remains constant while both cure time and residual scorch time vary with the heat history of the batch. The experiments fall into two groups. In the first group we have studied a large number of batches of the same two compounds and have developed the pattern. In the second we have studied a few batches each of nine compounds with five different accelerators to see if they fit the same pattern.

Heat history is a term used to indicate the cumulative time-temperature effect to which a rubber stock has been submitted. It is an integration of the time and temperature to which the stock has been exposed. It depends on the temperature of mixing, warm-up, calendering, and tubing. These temperatures in turn depend on the rate of processing, the temperatures of the cooling water, the cooling efficiency of the equipment, and the stock temperature best suited for a particular operation. Heat history also depends on the efficiency of cooling of the stock between sheeting and piling on skids. Air temperatures influence both the rate and extent of cooling. The time element is affected by rates of mixing, calendering, tubing, the length of time between operations, and any repetition of a process such as tubing.

Theoretically, heat history can be calculated as equivalent to a definite time at a definite temperature. In practice, of course, such calculations are difficult, if not impossible, to make with precision. However, rough estimates of probable heat history are regularly made by compounders. For example, to say that a stock must have a scorch time of 20 minutes at 250° F is to say that the heat history accumulated during processing may be equivalent to 20 minutes at 250° F.

Because of its importance to processing difficulties and to scrap stock, the effect of heat history is usually considered in relation to scorch time. Its effect on cure time is generally overlooked. In this study we have used the time of milling on a hot mill as a measure of the heat history of the batch. The stock temperature was measured with a needle pyrometer and kept within ±3° F of the temperatures designated.

It must be remembered that measurements of the type involved here are not high precision measurements and that the precision is further limited by the complications of mixing, curing, and remilling the compounds. The selection of scorch time and cure time of a batch on the mill or from press-cured sheets is, to some extent, a matter of personal judgment. We have taken considerable pains, both in the conduct of the experimental work and in the analysis of the

data, to overcome these handicaps as much as possible. We feel that the results are essentially accurate if not very precise.

MEASUREMENTS OF SCORCH TIME

The scorch times were measured in three different ways: (1) on the Mooney machine, (2) on a hot mill, and (3) by press cures.

Figure 2 shows a typical Mooney cure curve and how we construct it from laboratory data. The cure curve drawn by the recorder is generally too long for convenient use. Therefore, we take from this curve the six figures shown, as follows:

M minimum viscosity reading.
Tm time in minutes for the last minimum viscosity reading.
T2 time in minutes for the viscosity to rise 2 points.
T5 time in minutes for the viscosity to rise 5 points.
T10 time in minutes for the viscosity to rise 10 points.
T35 time in minutes for the viscosity to rise 35 points.

From these figures, it is easy to reconstruct the cure curve on a suitable scale, as is done in Figure 2. T5 is taken as the scorch time and is the time in minutes from the instant the dies are closed until the viscosity has risen 5 points[1] (ASTM D1077-49T). The Mooney cure time is taken as T35, the time for the viscosity

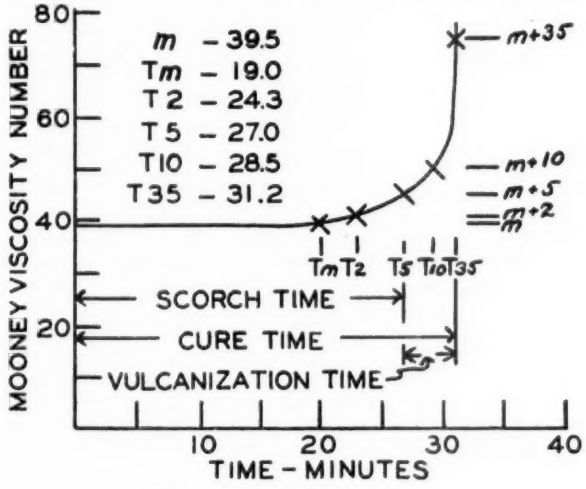


FIG. 2.—Typical Mooney cure curve.

to rise 35 points. The difference between the cure time and the scorch time is the vulcanization time. With slight modification, this is the method of Shearer, Juve, and Musch[2].

The mill scorch time is the time on a hot mill at which the stock shows definite signs of scorch. Smoothly milling stocks begin to get grainy, rough, or dry. The press scorch time was taken from a series of cures run at one-minute intervals. The time selected was that of the last cure before there was a definite rise in modulus and tensile strength.

TABLE I

BASE COMPOUNDS

Compound	A	B
Smoked sheet	100	100
Stearic acid	1	1
Antioxidant	1	1
Zinc oxide	10	10
Soft clay	50	50
Precipitated whiting	75	75
Ground whiting	60	60
Sun-checking wax	3	3
Sulfur	1	1
Ethylac	1.5	1.5
SA 62-O	—	0.2
	302.5	302.7

The two compounds used are shown in Table I. They are typical 30 per cent Hevea, wire-insulation stocks. Compound A is accelerated with Ethylac and Compound B with a mixture of Ethylac and SA 62 (tetraethylthiuram disulfide).

Table II shows the scorch times found by the three different methods for Compound A. The first column shows the Mooney scorch times determined at

TABLE II

SCORCH DATA FOR COMPOUND A AT 244° F

Mooney scorch	Mill scorch	Press scorch
26.9	56*	24*
28.6	72	26*
27.0	62	24*

* Calculated from 262° F.

244° F for three different batches. In the second column the first batch had a mill scorch time of 28 minutes at 262° F, which is equivalent to 56 minutes at 244° F. The other two mill scorch times were determined at 244° F. The press scorch times were all determined at 262° F, and doubled to give the equivalent scorch times at 244° F. The Mooney scorch time and the press scorch time are close together, but the mill scorch time is much longer.

TABLE III

SCORCH DATA FOR COMPOUND A AFTER REMILLING

Min. remilling at 244° F	Mooney scorch at 244° F	Total scorch equivalent at 244° F
0	28.6	28.6
52	21.9	73.9
62	13.3	75.3
68	6.7	74.7
72 S	—	72.0
Min. remilling at 262° F		
0	26.9	26.9
18	16.7	52.7
23	7.1	53.1
26	9.7	61.7
28 S	—	56.0

Table III shows how the scorch time varies for Compound A after different periods of hot milling. The first column shows the actual time of remill at 244° F. The stock was scorched in 72 minutes. The top figure is the maximum scorch time and the other figures are the values found after the periods of hot milling. The last column, the total scorch equivalent, is the sum of the first two columns. In each case, hot milling has appreciably lengthened the time of the total scorch equivalent. This means that the stock took longer to scorch on the hot mill than it did in the Mooney machine.

TABLE IV

SCORCH DATA FOR COMPOUND B AT 244° F

Mooney scorch	Mill scorch	Press scorch
12.2	17.0	12.0*
15.0	18.0*	14.0*
13.0	20.0	10.0*
13.9	20.0*	10.0*

* Calculated from 262° F.

The lower set of figures shows the same thing. Here the remilling temperature was 262° F, and the times were doubled to get the total scorch equivalents. This assumes a temperature coefficient of 2 for each 18° F.

Table IV shows the three types of scorch data for Compound B. Here again the press scorch time and the Mooney scorch time are close together, with the press scorch time a little shorter. The mill scorch time is somewhat longer, but the difference is not as great as for Compound A.

Table V shows the effect of hot milling on scorch time for Compound B, and is comparable to Table III. The upper values were all determined at 244° F,

TABLE V

SCORCH DATA FOR COMPOUND B AFTER REMILLING

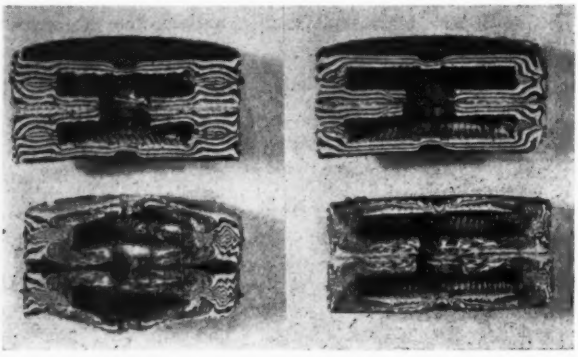
Min. remilling at 244° F	Mooney scorch at 244° F	Total scorch equivalent at 244° F
None	12.2	12.2
9	8.4	17.4
15	3.3	18.3
17 S	—	17.0
Min. remilling at 262° F		
None	15.0	15.0
6	6.2	18.2
9	2.7	20.7
10 S	—	20.0

and the total scorch equivalents are the sum of the other two values. For the lower set of figures the remilling was at 262° F, and the total scorch equivalent values are the sum of twice this value and the value for scorch at 244° F. The total scorch equivalent is somewhat longer where the stock has been remilled.

With Compound A, the press scorch time, where the stock was at rest, was much shorter than the mill scorch time, where the stock was being worked. Apparently, working delayed the onset of scorching. Since the Mooney scorch time was close to the press scorch time, the question arose as to just how much working the stock gets in the Mooney machine. The answer is indicated in

Figure 3, where we used alternating plies of black and white stock to build up the specimens. The black stock was the white one, to which 3 PHR of soft black had been added.

Figure 3a is with the small rotor. The top specimen was cured without turning the rotor. The bottom specimen was run by the usual procedure, but left in the machine at the end to get a tighter cure. The middle layers between the rotor and the die have been worked, but on the sides and next to the rotor and dies, the stock has not been worked. Figure 3b shows corresponding



A B

FIG. 3—Specimens made with small (left) and large (right) rotors.

specimens with the large rotor. The pattern is a little different because of the knurling on the edge of the rotor, but again only part of the stock has been worked.

SCORCH TIME, CURE TIME, AND VULCANIZATION TIME

We have seen that the scorch time is shortened as a result of hot milling. The next question is: How does hot milling affect cure time and vulcanization time?

Table VI shows how press-cure time is affected by hot milling. In determining cure times, cures were made at one minute intervals. The first cure to

TABLE VI

PRESS CURE TIME AFTER REMILLING—COMPOUND A

Min. remilling at 244° F	Press-cure time (min. at 262° F)
None	17
30	14
40	12
50	11
Min. remilling at 262° F	
None	18
18	14
23	12
26	10

TABLE VII

PRESS CURE AFTER REMILLING—COMPOUND B

Min. remilling at 244° F	Press-cure time (min. at 262° F)
None	10
9	9
15	7
17	6
Min. remilling at 262° F	
None	9
3	8
5	7
8	5

show a modulus at 200 per cent of 400 lbs. per sq. in. and a tensile strength of 1700 lb. per sq. in. was taken as a good technical cure. The cure time is markedly affected by heat history, as measured by time on a hot mill. Table VII shows corresponding data for Compound B. Again heat history has a pronounced effect on cure time. These results are typical of many which we have obtained.

In the comparison of vulcanization time with scorch and cure times, we can use Mooney data, press-cure data, or combinations of the two. We repeat that what we call the vulcanization time is the difference between the cure time and the scorch time.

Figure 4 shows a scattergram in which Mooney scorch time has been plotted against Mooney vulcanization time for Compound A. The data cover 52 batches, mixed over a period of 18 months using three lots of rubber. The variations in scorch time are the results of different mixings and of different times and temperatures of hot remilling. There is no regular change in vulcanization time as the scorch time changes. On the other hand, all of the vulcanization times fall within a rather narrow band. Figure 5 shows the dis-

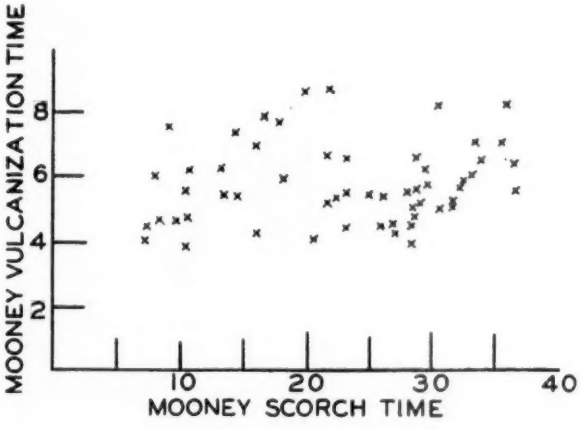


FIG. 4.—Mooney scorch time vs. Mooney vulcanization time for 52 batches of Compound A.

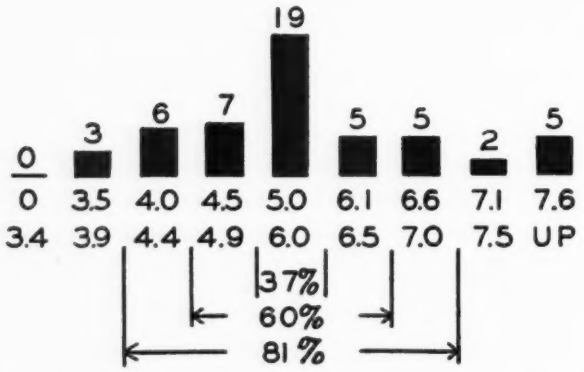


FIG. 5.—Distribution of Mooney vulcanization times (at 244° F) for 52 batches of Compound A.

tribution of the Mooney vulcanization times for these same batches. Although the scorch times varied from 6.5 minutes to 36.5 minutes, 81 per cent of the vulcanization times were within the range of 5.5 ± 1.5 minutes.

Figure 6 shows the scattergram for Mooney vulcanization time vs. Mooney scorch time for 37 batches of Compound B. Again there is no regular variation of vulcanization time with scorch time, and again the vulcanization times all fall within a narrow band. Figure 7 shows the distribution of the vulcanization times for Compound B. Although the scorch times varied between 21.2 and

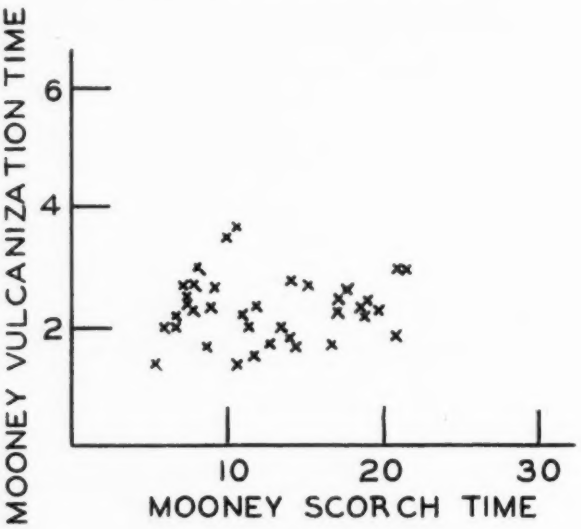


FIG. 6.—Mooney scorch time vs. Mooney vulcanization time for 37 batches of Compound B.

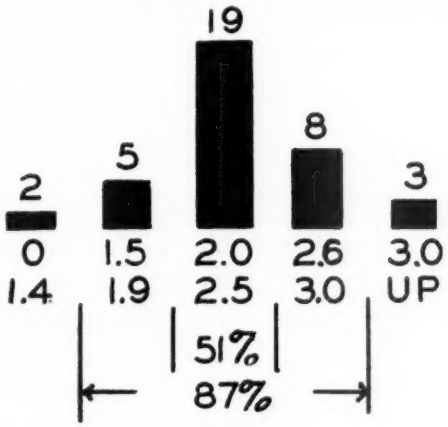


FIG. 7.—Distribution of Mooney vulcanization times (at 244° F) for 37 batches of Compound B.

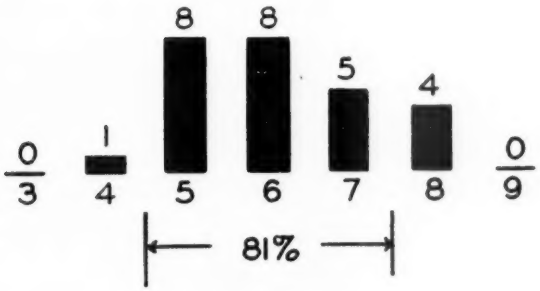


FIG. 8.—Distribution of press vulcanization times (at 262° F) for 26 batches of Compound A.

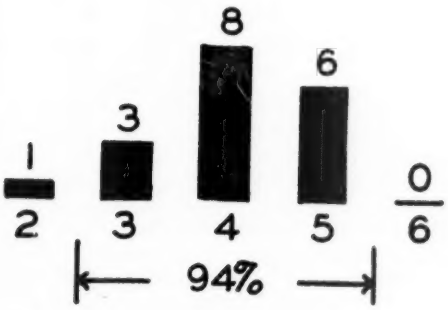


FIG. 9.—Distribution of press vulcanization times (at 262° F) for 18 batches of Compound B.

5.8 minutes 87 per cent of the vulcanization times fall in the range of 2.25 ± 0.75 minutes.

Figure 8 shows the distribution of press vulcanization times at 262° F for 26 batches of Compound A. These values were obtained by subtracting the press cure time from the press scorch time. Here 81 per cent of the values fall in the range of 6 ± 1 minute. Figure 9 shows the corresponding data for 18

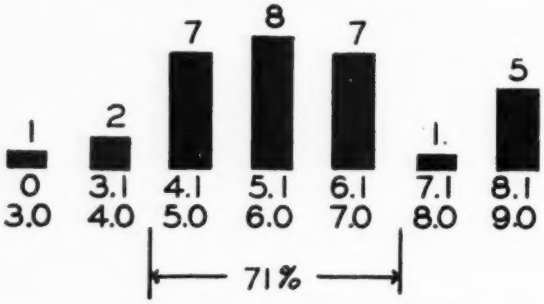


FIG. 10.—Distribution of calculated vulcanized times for 31 batches of Compound A.

batches of Compound B. Here 94 per cent of the values fall in the range of 4 ± 1 minute.

The vulcanization times at 262° F were also calculated by using the press-cure time at 262° F and subtracting the Mooney scorch time measured at 262° F or calculated to 262° F from the data obtained at 244° F. Figure 10 shows the results for 31 batches of Compound A, calculated in this manner. Here 71 per

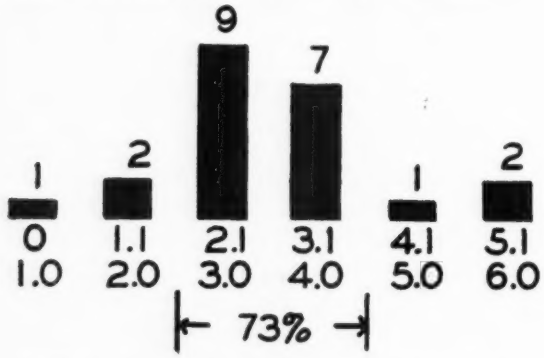


FIG. 11.—Distribution of calculated vulcanization times for 22 batches of Compound B.

cent of the results fall in the range of 5.5 ± 1.5 minutes. Figure 11 shows similar data for 22 mixes of Compound B. Here 73 per cent of the results are in the range of 3 ± 1 minute. These results indicate that, for each compound, the vulcanization time is constant within narrow limits regardless of the scorch time.

It is very difficult to obtain high precision in this type of work. In spite of all our efforts, there are some individual results which are out of line, and the

quantitative agreement between batches mixed at different times on the same recipe leaves something to be desired. However, every series of experiments showed the same relation between scorch time, cure time, and hot mill time. The statistical comparisons cover 89 batches mixed at different times over a period of some 18 months, with different pigments, and with three different lots of blended rubber.

The second phase of our work covered experiments to see if similar results would be obtained with a wider range of acceleration. Here we used five different accelerators in nine different compounds with the base recipe shown in Table VIII. A large batch of each compound was mixed, and portions of it were remilled for various periods of time at 262° F.

Table IX shows how Mooney scorch time is affected by time on a hot mill. For the three compounds with varying ratios of Ethylac and sulfur the scorch time decreases with hot remill time. In this case, as shown by the total scorch equivalent, the hot mill time, or mill scorch time, is considerably longer than the corresponding Mooney scorch time. With the two compounds containing SA 52 (tetramethylthiuram disulfide), mill scorch time is equal to Mooney scorch time. The same is true with SA 62, with MBT and with MBTS. In every case the scorch time decreased with increasing time of remilling.

TABLE VIII

MASTERBATCH RECIPE

Smoked sheet blend	100
MT black	40
Zinc oxide	5
Stearic acid	2
PBNA	1
	148

The cure time also decreased with increasing heat history as measured by time on the hot mill. This is shown by Table X.

Thus we see that in all these compounds both scorch time and cure time are variable. How about the vulcanization times? This is shown by Table XI, using two methods of estimating vulcanization time. The Mooney vulcanization time is T35 minus T5. The press vulcanization time at 280° F is the press cure time at 280° F, minus Mooney scorch time calculated to 280° F (*e.g.*, one-fourth of the Mooney scorch time at 244° F). In all cases vulcanization times were quite constant within each group.

This limited study of the nine compounds indicates that all of them fall into the pattern shown by the extensive study of the first two compounds.

Table XII is a comparison of the maximum scorch times and the vulcanization times for these compounds. With only these five accelerators there can be considerable differences in the ratios of vulcanization time to maximum scorch time. The two C compounds have a shorter vulcanization time and also a shorter scorch time than the two D compounds. Compound B-1 has the same vulcanization time as Compound F-1 but a much longer scorch time. Compound D-1 has about the same scorch time as Compound G-1 but a much shorter vulcanization time. The ratio of maximum scorch time to vulcanization time ranges from 1.4 in Compound F-1, through 2.0 for Compound G-1 and 4.3 for Compound C-1 to 5.4 for Compound B.3.

Now let us look again at our idealized curve (Figure 1). With each of these natural-rubber compounds, the vulcanization time is constant. With different

TABLE IX

SCORCH DATA FOR VARIOUS COMPOUNDS AFTER REMILLING

Min. remilling at 262° F	Mooney scorch at 244° F	Total scorch equivalent at 244° F
	Compound B-1—Ethylac 1.5-sulfur 1.0	
0	27.0	27.0
12	23.2	47.2
17	18.5	52.5
19	9.9	47.9
22	scorch	44.0
	Compound B-2—Ethylac 1.0-sulfur 1.5	
0	29.5	29.5
13	16.9	42.9
18	10.7	46.7
20	7.8	47.8
23	scorch	46.0
	Compound B-3—Ethylac 0.5-sulfur 2.5	
0	26.8	26.8
6	18.6	30.6
11	15.3	37.3
13	13.0	39.0
16	scorch	32.0
	Compound C-1—SA 52 1.0-sulfur 1.0	
0	13.0	13.0
2	9.9	13.9
4	8.2	16.2
5	5.7	15.7
7	scorch	14.0
	Compound C-2—SA 52 0.4-sulfur 2.5	
0	13.6	13.6
3	9.8	15.8
5	7.0	17.0
7	4.6	18.6
8	scorch	16.0
	Compound D-1—SA 62 1.0-sulfur 1.0	
0	20.2	20.2
3	16.0	22.0
5	11.3	21.3
7	6.3	20.3
10	scorch	29.0
	Compound D-2—SA 62 0.4-sulfur 2.5	
0	22.6	22.6
3	15.0	21.0
8	9.0	25.0
10	6.4	26.4
12	scorch	24.0
	Compound F-1—MBT 0.75-sulfur 2.5	
0	10.4	10.4
2	10.0	14.0
3	6.6	12.6
4	6.7	14.7
5	scorch	10.0
	Compound G-1—MBTS 1.0-sulfur 3.0	
0	19.5	19.5
4	12.8	20.8
6	12.0	24.0
8	9.7	25.7
11	scorch	22.0

TABLE X

CURE TIME FOR VARIOUS COMPOUNDS AFTER REMILLING

Min. remilling at 262° F	Press-cure time (min. at 280° F)
Compound B-1—Ethylac 1.5-sulfur 1.0	
0	14
12	13
17	12
19	10
22	—
Compound B-2—Ethylac 1.0-sulfur 1.5	
0	13
13	11
18	9
20	8
23	—
Compound B-3—Ethylac 0.5-sulfur 2.5	
0	11
6	10
11	9
13	9
16	—
Compound C-1—SA 52 1.0-sulfur 1.0	
0	6
2	6
4	5
5	5
7	—
Compound C-2—SA 52 0.4-sulfur 2.5	
0	7
3	6
5	4
7	3
10	—
Compound D-1—SA 62 1.0-sulfur 1.0	
0	9
3	9
5	8
7	6
10	—
Compound D-2—SA 62 0.4-sulfur 2.5	
0	9
3	9
8	6
10	5
13	—
Compound F-1—MBT 0.75-sulfur 2.5	
0	10
2	10
3	10
4	8
5	—
Compound G-1—MBTS 1.0-sulfur 3.0	
0	16
4	14
6	12
8	12
11	—

TABLE XI

VULCANIZATION TIME FOR VARIOUS COMPOUNDS

Min. remilling at 262° F	Mooney at 244° F	Press at 280° F
	Compound B-1—Ethylac 1.0-sulfur 1.5	
0	7.2	7.25
12	9.0	7.25
17	6.5	7.50
19	6.7	7.50
22	—	—
	Compound B-2—Ethylac 1.5-sulfur 1.0	
0	6.4	6.50
13	6.7	6.75
18	6.9	6.25
20	5.4	6.00
23	—	—
	Compound B-3—Ethylac 0.5-sulfur 2.5	
0	5.4	4.25
6	7.1	5.25
11	7.5	5.00
13	5.5	5.25
16	—	—
	Compound C-1—SA 52 1.0-sulfur 1.0	
0	4.4	2.25
2	4.5	3.50
4	4.5	3.00
5	4.6	3.50
7	—	—
	Compound C-2—SA 52 0.4-sulfur 2.5	
0	4.6	3.60
3	3.4	3.50
5	4.1	2.25
7	3.4	2.00
10	—	—
	Compound D-1—SA 62 1.0-sulfur 1.0	
0	6.6	4.00
3	7.0	5.00
5	7.0	5.00
7	5.8	4.50
10	—	—
	Compound D-2—SA 62 0.4-sulfur 2.5	
0	4.9	4.50
3	4.1	5.25
8	4.1	3.75
10	3.8	3.50
13	—	—
	Compound F-1—MBT 0.75-sulfur 2.5	
0	2.1	7.40
2	4.0	7.50
3	2.9	8.40
4	2.8	6.40
5	—	—
	Compound G-1—MBTS 1.0-sulfur 3.0	
0	6.4	11.00
4	5.7	10.25
6	7.0	9.00
8	5.3	9.25
11	—	—

TABLE XII

COMPARISON OF MAXIMUM SCORCH TIMES AND VULCANIZATION TIMES FOR VARIOUS COMPOUNDS

Accelerator	Compound	Scorch time at 244° F		Vulcanization time press at 280° F
		Mooney	Mill	
Ethylac	B-1	27.0	44.0	7.4
	B-2	29.5	46.0	6.4
	B-3	26.8	32.0	5.0
SA 52	C-1	13.0	14.0	3.0
	C-2	13.6	16.0	2.8
SA 62	D-1	20.2	20.0	4.6
	D-2	22.6	24.0	4.4
MBT	F-1	10.4	10.0	7.4
MBTS	G-1	19.5	22.0	9.9

compounds, especially with different accelerators, the vulcanization times may be different and so may the maximum scorch times. Further, the differences in scorch time may be independent of those in vulcanization time. It is, therefore, possible to get many different combinations of maximum scorch time and vulcanization time.

The scorch time shown on the curve represents the maximum available. Part or all of it may be used up by the heat history built up during processing. Thus, after processing the residual scorch time is considerably shorter. The vulcanization time, however, remains constant. Now, since the residual scorch time varies with the heat history and the vulcanization time remains constant, it follows that the cure time also must vary with the heat history.

SIGNIFICANCE TO COMPOUNDING AND PROCESSING

Now let us consider the significance of these results to the compounding and processing of rubber.

There are a number of variables in factory processing which can result in considerably different heat histories for different batches of the same compound: variation in room temperature or the temperature of the cooling water, the difference between the start up on cold equipment and the last batch of a run when the equipment is hot, efficiency of cooling batch stock before it is stacked on a skid, or an extra pass or two through a tube machine.

For example, suppose two skids are loaded with batch stock. In one case the average stock temperature is 217° F, in the other it is 199° F. If we assume that the average temperature of the first skid drops to 199° F in one hour, the difference in heat history, for the stock on the two skids, is equivalent to about 7 minutes at 262° F.

Under the pressure for production, factory cures are often made as short as possible. If the factory cure for Compound A (Table VI) were set on the basis of batches with a heat history equivalent to 20 to 25 minutes at 262° F, it might well be set at 12 minutes at 262° F. If, for some reason, such as cold winter weather or a quick easy run, the heat history dropped to an equivalent of 10 to 15 minutes at 262° F, the product would come out with an undercure, and some compounder would start tearing his hair.

With faster curing compounds, such as Compound B (Table VII), this source of difficulty could be even more pronounced. In the first place, such compounds are generally used where a minimum cure time is desired, and in

the second place, small variations in heat history have a greater effect on cure time.

There is another consequence of this constancy of vulcanization time which is interesting, if not immediately practical. Compounders often say they want an accelerator which will process safely at curing temperature. This is quite feasible from a compounding viewpoint. All that is necessary is to have factory processing so controlled that each batch of compound has essentially the same heat history.

In Figure 1 we have scorch time and vulcanization time at the same temperature. It is possible to use up all the scorch time in processing and then cure in the vulcanization time. The object is to put the product into the cure just before the end of the scorch time. That this can actually be done is shown by the results given in Table XIII.

TABLE XIII

PROCESSING TIME VS. CURING TIME AT THE SAME TEMPERATURE

Compound A			Compound B	
Process time	Cure time	Temp.	Process time	Cure time
24 min.	12 min.	262° F*	8 min.	6 min.
12 min.	6 min.	280° F†	4 min.	3 min.
6 min.	3 min.	300° F†	2 min.	1.5 min.

* Experimental.
† Calculated.

First, take Compound A. This stock was remilled for 24 minutes at 262° F, and showed no signs of scorch. It was then cured in a press and reached full technical cure in 12 minutes at 262° F. At the same temperature of 262° F, it could be milled safely for twice as long as it took to reach full cure in the press. The values which show the two corresponding times at temperatures of 280° and 300° F were calculated from those at 262° F. They indicate that the stock can be milled 12 minutes at 280° F and cured in 6 minutes at 280° F. Also, you might mill for 12 minutes at 280° F and cure in 12 minutes at 262° F.

On the other side, we have the corresponding figures for Compound B. It was actually milled 8 minutes at 262° F, then cured in 6 minutes at 262° F. Again, the other four figures, were calculated from the experimental results at 262° F.

CONCLUSIONS

To summarize, the following hold true for natural rubber:

(1) Each compound has a characteristic maximum scorch time, vulcanization time, and cure time, which depend chiefly on the accelerator.

(2) For any given batch of compound, both scorch time and cure time are shortened by an amount equivalent to the processing heat history of the batch.

(3) The vulcanization time remains constant.

(4) These relations help to explain variations in factory cures and indicate the advantages of close control of heat history in factory processing.

REFERENCES

[1] ASTM Standards 1952, Vol. 6, p. 483, ASTM D1077-49T.
[2] Shearer, Juve, and Musch, *India Rubber World* **117**, 216 (1947).

FLEX-CRACKING AND CRACK GROWTH TESTS SOME IMPORTANT FACTORS *

J. M. BUIST

RUBBER SERVICE DEPARTMENT, DYESTUFFS DIVISION, IMPERIAL CHEMICAL INDUSTRIES LTD., HEXAGON HOUSE, BLACKLEY, MANCHESTER, ENGLAND

INTRODUCTION

Flex-cracking has been a major cause of failure in rubber articles for many years and since the early 1930's various test methods have been suggested. The whole subject of the mechanism of flex-cracking and flex-cracking tests was reviewed recently[1], and in 1950 Committee ISO/TC/45 agreed that only the De Mattia machine should be considered for international standardization and that the question of crack growth should be tackled before flex-cracking. Cooperative tests, following the suggested crack-growth procedure, are being carried out in nine laboratories, four laboratories in the United Kingdom, one in Austria, one in France, one in Holland, one in Italy, and one in the United States. Preliminary results show that agreement between laboratories is not good and support the view that the greatest possible care and attention must be given to experimental details if reproducible and comparable results are to be obtained in different laboratories.

In the earlier paper[1] referred to above, three important aspects of accuracy of testing are defined as:

(*a*) the accuracy of the measurement of flex-cracking and crack-growth resistance of any one sample;
(*b*) the degree of reproducibility of the test conditions;
(*c*) the degree of reproducibility of the test-specimens.

Newton[2] and Buist and Williams[3] have shown, using the De Mattia and du Pont machines, respectively, that the error in measurement is considerably less than the errors associated with the test conditions and the test-specimens. Further work is, therefore, clearly required to define more exactly the important factors in the test conditions and in the preparation of the test-specimens. In the present paper, data on the following factors are discussed:

(1) Temperature of test.
(2) Mean strain and dynamic strain.
(3) Method of preparing test-specimens.
(4) Methods of interpreting results.
(5) Methods of producing initial cut in crack-growth tests and in a final section the use of the De Mattia in testing flex-cracking and crack growth of tread and soling compounds is discussed.

EFFECT OF TEMPERATURE OF TEST

Previous reports on the effect of temperature are conflicting. For example, Somerville[4] found that the rate of cracking decreased with rise of temperature

* Reprinted from the Transactions of the *Institution of the Rubber Industry*, Vol. 29, No. 2, pages 72–91, April 1953.

with natural-rubber gum compounds, whereas Rainier and Gerke[5] reported that the rate of cracking of natural-rubber tread compounds increased with temperature. A De Mattia type of machine was used in both cases. Similarly conflicting evidence has been published on crack growth by Carlton and Reinbold[6] and by Breckley[7]. Efforts were, therefore, made to obtain additional information and crack growth was determined on a Flipper machine[8]. This machine was chosen since it was conveniently operated at an elevated temperature. No cooling facilities were available, and experience had shown that it was difficult to maintain a temperature near room temperature. The temperature range investigated, therefore, was 40–100° C. Only a limited number of compounds were examined, but the experiment provides information on the behavior of different polymers over a range of temperature.

FORMULATION OF THE COMPOUNDS

Tread type compounds were prepared from natural rubber, Neoprene Type GN, GR-S, Perbunan, and Butyl rubber.

Smoked sheet	100	—	—	—	—
Neoprene-GN	—	100	—	—	—
GR-S	—	—	100	—	—
Perbunan	—	—	—	100	—
Butyl rubber	—	—	—	—	100
MPC black	47.5	36	50	50	50
Stearic acid	3	2.5	1	2	—
Sulfur	3	—	2	1.5	2
Mercaptobenzothiazole	0.85	—	—	—	—
Magnesia	—	4	—	—	—
Tricresyl phosphate	—	2.5	—	—	—
Phenyl-β-naphthylamine	—	2	—	—	—
Pine tar	—	—	3	3	—
Vulcafor-F	—	—	1.6	1.2	—
Tetramethylthiuram disulfide	—	—	—	—	1
Zinc diethyldithiocarbainate	—	—	—	—	1.5
Zinc oxide	5	5	5	5	5
Cure at 141° C	60′	40′	90′	90′	90′/153° C

EXPERIMENTAL RESULTS

Six test-pieces were tested from each compound, the cracks being initiated by the insertion of an incision, 1 mm. long, in the center of the groove. The length of the crack was measured at frequent intervals until it had extended to the full length of the groove.

The relationship between the length of groove and time of flexing at each temperature is given in Figures 1 and 2, the results quoted being the median of the six results. With the exception of Butyl rubber, which is discussed later, it was found that in all cases the rate of cracking increased with a rise of temperature.

One point of interest is found in the shape of the graphs. Natural rubber, GR-S, and Perbunan show positive curvature, while Neoprene-GN shows negative curvature. Butyl rubber is not as consistent and can be considered to give linear results on the average. Plotting the results on a logarithmic time scale (which is the same as using the logarithm of the number of flexing cycles) does not, in general, give a linear graph. Because of the differences in curvature obtained with different rubbers, it is apparent that there is no universal mathematical treatment which can be applied to all types of rubber.

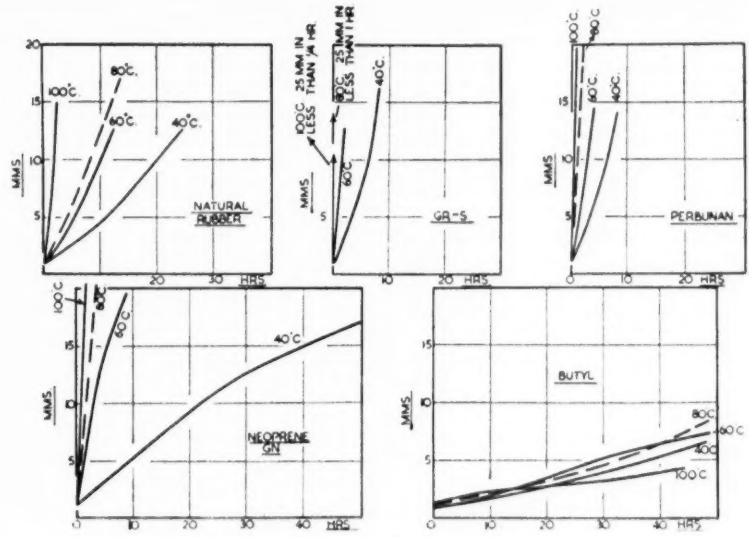


FIG. 1.—Effect of temperature on crack growth.

Butyl rubber is outstanding in resistance to crack growth and is not greatly affected by temperature. There is some evidence that the rate of growth tends to become faster on increasing the temperature from 40 to 60° C (or 80° C), but is slightly slower at 100° C. The differences are of doubtful significance but could be explained in terms of tension set becoming appreciable at higher temperatures.

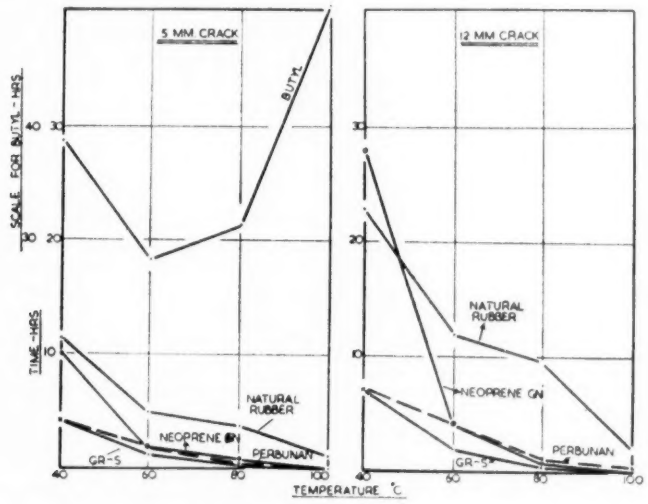


FIG. 2.—Effect of temperature on crack growth.

Neoprene-GN and natural rubber crack at a similar rate at 40° C, but Neoprene-GN is definitely inferior at higher temperatures. The comparison of these rubbers is complicated by the different curvature of the graphs. In the case of natural rubber, the rate of cracking becomes faster as the crack grows, whereas with Neoprene-GN it becomes slower. Hence a Neoprene-GN compound can crack initially at a similar rate to or even faster than a natural rubber compound, *e.g.*, at 40° C, and yet the ultimate life can be greater.

Both GR-S and Perbunan show rapid crack growth which is accelerated by a rise of temperature.

An approximate idea of the temperature coefficients is obtained from Figure 2, which indicates the effects of temperature on the time for the crack to grow to 5 and 12 mm. Since some of the results at 80° and 100° C have not been measured with precision, the relative rates at 40° and 60° C are taken to give the order of magnitude of the rates of cracking over this range of temperature. It will be noted, however, that in no case is the relationship between rate of cracking and temperature linear. The ratio of the flexing time at 40° to that at 60° C is quoted below:

Over this temperature range GR-S and particularly Neoprene-GN are most sensitive to temperature. Natural rubber and Perbunan have similar temperature coefficients and Butyl rubber a low temperature coefficient (which tends to be reversed in sign at high temperatures).

RATIOS

	5 mm. crack	12 mm. crack
Natural rubber	2.2	2.1
GR-S	4	3.5
Perbunan	2	1.75
Neoprene-GN	5	6
Butyl rubber	1.3	—

As a result of this work, Committee ISO/TC/45 recommended at the 1951 meeting at Oxford that "A close tolerance on the ambient temperature is not specified and tests are normally performed at room temperature, although elevated temperatures may often be used with advantage. There is some evidence that the rates of cracking of Neoprene-GN and of GR-S are particularly sensitive to the test temperatures, and in these cases it is suggested that the tolerance in temperature should be ±2° C."

MEAN STRAIN AND DYNAMIC STRAIN

Many early investigators[9] drew attention to the importance of fatigue in flex-cracking. They all found that if the sample returned to zero strain during a cycle, the rate of cracking was a maximum. This observation seems quite inadvertently to have retarded progress, since many experimenters have argued that fatigue effects should be separated from flex-cracking effects. The observation is of practical importance as, in service, longer life is undoubtedly attained if the article is not permitted to pass through zero strain. Nevertheless some fatigue normally occurs in most applications where flex-cracking is important, and therefore there is little point in trying to exclude it rigidly. In fact it may be preferable to choose the conditions of strain such that the maximum fatigue, rather than an unknown amount, occurs. Certainly a given flexing test should operate under conditions where there is a definite extension, return to zero strain, and, where possible, a definite compression; the testing conditions should

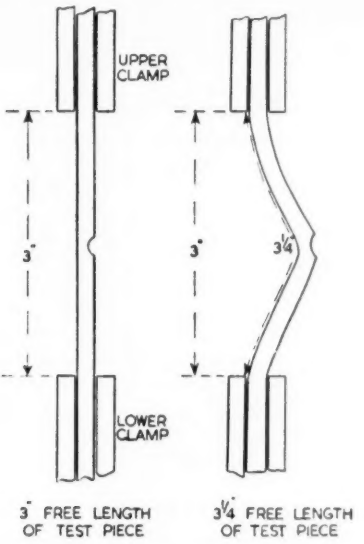


FIG. 3.—Effect of free length of test-piece.

never be such that small variations of the specified conditions can lead to the test-piece either returning to, or passing through, zero strain in cases where it is intended that the test-piece should always be under a positive strain.

In the De Mattia test, the mean strain and the dynamic strain are determined by:

(1) the relative setting of the fixed and movable clamps;
(2) the amplitude of movement of the moving clamp;
(3) the free length of test-piece between the clamps.

Although all three are specified in ASTM D430 and in B.S.903, there is ample evidence that the rate of flexing is markedly affected by small changes in any of the items. If, for example, items 1 and 2 are kept constant and item 3

TABLE 1

EFFECT OF FREE LENGTH OF TEST-PIECE

Compound	Free length: 3 inches, kilocycles for crack to reach 8 mm.	3 inches, kilocycles for crack to reach 15 mm.	3¼ inches, kilocycles for crack to reach 8 mm.	3¼ inches, kilocycles for crack to reach 15 mm.
Natural rubber tread Channel black + antioxidant	32.8	>170	2177	>6000
Natural rubber tread Furnace black + antioxidant	6.0	53.3	1305	>6000
GR-S tread 30′ cure	7.4	21.5	11.7	40.0
GR-S tread 60′ cure	4.2	14.7	8.5	25.7

is altered so that the free length of test-piece is varied from $3\frac{1}{4}$ to 3 inches (*cf.*, Figure 3), the following crack growth results are obtained:

Further, it has been observed that when the free length of the test-piece is a nominal 3 inches, a variation of less than 0.1 inch in the distance between the clamps (which simultaneously gives a variation in free length of the same magnitude) causes an obvious change in rate of crack growth. The rate of flex-cracking increases with an increase in the distance between the jaws. Similarly it has commonly been observed that even when a double sided machine is adjusted as accurately as possible, significantly different results can be obtained on the two sides. When the free length of the test-piece is 3 inches, the test-piece returns to zero strain in each cycle if the other test conditions agree with those laid down in ASTM D430 and B.S.903. The above results show that the effect of free length of test-piece is more pronounced with natural rubber compounds than with GR-S compounds. This observation agrees with work of Holt and Knox[10], who compared thirteen methods of measuring crack growth and concluded that the severity of the test was increased with rubbers which crystallize if the strain passed through zero in a flexing cycle. Another conclusion of these authors, however, namely, that with rubbers which do not crystallize, such as GR-S, the passing through zero strain seems to be of no

TABLE 2

EFFECT OF FREE LENGTH OF TEST-PIECE ON STRAIN

	Free length of test-piece		
	3 in.	$3\frac{1}{4}$ in.	$3\frac{1}{2}$ in.
No. of kilocycles to grow to 8 mm.	5.65	8.85	24.75
Minimum strain	0	39%	57%
Maximum strain attained during flexing	136%	164%	153%
Strain range	136%	126%	97%

particular significance, is not borne out by the above results. The effects noted with GR-S in the present paper are certainly significant and of practical importance.

These observations illustrate the importance of controlling the mechanical features of the test with great accuracy, and they suggest that it may be extremely difficult to control these factors with the machines now available, unless new methods are devised for carrying out the adjustments. The use of jigs for positioning test-pieces before insertion in the machine may lead to improvement.

The effect of the free length of the test-piece has been confirmed by several separate experiments and on every occasion it has been demonstrated that the rate of cracking decreases as the free length of the test piece increases. In certain experiments the effect is not so pronounced as noted above. For example, results obtained for the number of kilocycles for a crack to grow to 8 mm. with a natural-rubber tread compound containing channel black but no antioxidant are given below.

Before discussing the above results it must be stressed that the measurements of surface strain are difficult to carry out with a high degree of accuracy, but it is believed that the error associated with the above measurements is not higher than 5 per cent.

The largest difference of rate of cracking occurs when the free length of test-piece is altered from $3\frac{1}{8}$ to $3\frac{1}{4}$ inches, and one explanation is that the range of

strain imposed on the test-piece during flexing is reduced by about 30 per cent when the free length is increased to $3\frac{1}{4}$ inch. Another point of explanation is that Rainier and Gerke[5] found that between the limits of a positive minimum and a given maximum strain the rate of growth was slower the greater the value of the minimum. The difference in results between a free length of 3 and $3\frac{1}{8}$ inches can hardly be due to the small difference of range of strains, and is much more likely to be due to the fact that with a free length of 3 inches the static strain is zero and the test-piece returns to zero strain during each cycle.

The above results do suggest, however, that it is unfortunate that American and British test specifications for the De Mattia method have chosen $3\frac{1}{4}$ inches as the free length of the test-piece. Small variations of this length ($3\frac{1}{4}$ inches), produce very large variations of the rate of cracking. It appears that a free length of 3 inches would be more suitable as small variations in the free length of test-piece about this region (3 inches) have less effect on the rate of cracking, which is increased due to having the optimum conditions for fatigue and also a higher range of imposed strain. This conclusion is supported by the work of Rainier and Gerke[5], who reported that, when the minimum strain was almost zero, the rate of growth was nearly constant and independent of the degree of cracking up to 60 per cent deterioration.

There are a number of essential requirements which an agreed test for crack growth measurement should possess and which are worth listing. These are:

(*a*) It should be possible to complete the test with a "normal" rubber compound in a "reasonable" time, *e.g.*, in less than 100 Kc.
(*b*) The rate of crack growth should be sufficiently great for the test to be completed before the appearance of subsidiary cracks, which alter the stress distribution and confuse the appearance of the test-piece. In an extreme case, cracks starting from the edge of the test-piece could join with the principal crack before it has attained the maximum specified length.
(*c*) The initial crack should be propagated as an unique crack.

A suggestion of Rainier and Gerke[5] has a bearing on requirements (*a*) and (*b*). They reported a linear breakdown of the test-piece provided the degree of deterioration does not exceed 60 per cent. Little attention appears to have been paid to this statement, but it raises the question of whether the suggested I.S.O. final crack length of 15 mm. may not be too great. If the test were terminated earlier it would give a shorter and more convenient test and would help to eliminate the effect of additional cracks starting spontaneously, particularly from the edge of the test-piece. The present author would suggest that crack initiation should be measured by the Kc. required for an initial crack of 2 mm. to reach 4 mm., and crack growth by the Kc. required for the 4 mm. crack to grow to 8 mm.

The above requirements for a suitable crack growth test are not met at present using the De Mattia test

METHOD OF PREPARING TEST-SPECIMENS

In 1951 a comparison was carried out between test-pieces prepared (*a*) by molding in a multicavity mold and (*b*) by cutting from a sheet in which is molded a groove of standard dimensions. This was done to enable a decision

to be made as to whether these two alternatives could be included in any international method employing the De Mattia machine.

The results of this first test were that the cut test-pieces showed significantly greater flexing resistance than the molded test-pieces[11]. It was felt that the experiment should be repeated for both flex-cracking and crack growth since an inevitable shortcoming of the above experiment was the fact that two entirely different molds were used for the test. The mold used to prepare the sheet was an old De Mattia multiple cavity mold, with the separating walls removed. A separate multicavity mold was used to prepare the molded test-

TABLE 3

FLEX-CRACKING RESULTS (KILOCYCLES)

	Pin-holes	Slight cracks	Medium cracks	Deep cracks	Graphical method: Initiation	Graphical method: Propagation
Molded test-pieces mold 1	77	239	325	375	90	295
Molded test-pieces mold 2	85	135	203	248	70	174
Test-pieces cut from molded sheet	81	212	280	357	87	260

pieces. Another question which had to be answered was whether the difference observed between the two types of test-piece was greater than would be found between test-pieces prepared in different molds.

Further work was therefore done with the above two molds and an additional multicavity mold; flex-cracking and crack growth tests were carried out on a De Mattia machine with a free length of test-piece of $3\frac{1}{4}$ inches. The results for four stages of cracking—pinholes, slight cracks, medium cracks, deep cracks[3]—are given in Table 3. The initial cut in the test-pieces for crack growth was made with the chisel tool which has been suggested for international standardization[12], and the crack growth results are given in Table 4.

TABLE 4

CRACK GROWTH

Kilocycles for crack to grow to	5 mm.	8 mm.	10 mm.
Molded test-pieces mold 1	21.7	53.6	121.1
Molded test-pieces mold 2	12.9	31.9	53.6
Test-pieces cut from molded sheet	17.9	34.4	71.9

A full analysis of the individual results obtained has been carried out and this analysis leads to the following conclusions:

(1) there is no significant difference between flex-cracking results (or crack growth results) on test-pieces prepared by molding in two different multicavity molds.
(2) there is no significant difference between flex-cracking results (or crack growth results) on test-pieces cut from a molded sheet or test-pieces molded in a multicavity mold.

Both methods of preparing test-pieces can, therefore, be included as alternative procedures in a national or international specification for flex-cracking or crack-growth tests using the De Mattia machine. The reason why such apparently large differences between molds are not significant is, of course, because errors due to other causes are so large. It is noteworthy that in both the flex-cracking and crack-growth tests the three molds are placed in the same

relative order. There seems little doubt that the differences would prove to be significant if a larger number of test-pieces had been used, but it follows that where only a relatively small number of replicate test-pieces are employed, *e.g.*, 4 to 8; the errors are probably of such a magnitude that differences between molds are not of significance. Another important observation however is that the difference between the two multicavity molds is greater than the difference between samples cut from sheet and those prepared in a multicavity mold.

METHODS OF INTERPRETING FLEX-CRACKING AND CRACK-GROWTH RESULTS

The treatment of flex-cracking results has recently been discussed fully[3], and it is accepted that two quantities must be measured, one being the period of flexing or number of flexures and the other "the degree of flex-cracking". The degree of cracking is normally defined by certain specific stages of breakdown illustrated by means of standard samples or photographs. It is possible to construct a series of samples covering a range of cracking so that the samples are equally and regularly spaced as judged by visual assessment. Under these conditions Newton[13] claims that the number of flexures to produce each successive grade of cracking increases in an exponential fashion, and there is, therefore, a linear relationship between the grade number and the logarithm of the number of flexures when the grades are numbered consecutively.

Buist and Williams[3] pointed out cases where Newton's logarithmic method was not always satisfactory, and they suggested a graphical method of treating the results. With the graphical method random variations in results are ignored, and average flex-cracking results obtained. It is of interest to compare the two methods of treating results, using the same basic data. The data used for the comparison were taken from a paper by Newton and Scott[14]. The graphical method of assessment has its chief value for comparing rubbers tested in one experiment. The results quoted in the paper by Newton and Scott have been sub-divided into five lots (A, B, C, D, E), representing test-pieces vulcanized on different days. The results used were those obtained with samples numbered 1–25 (Table 1), the lots A to E being identified from Tables 4 and 5. All the results were, therefore, obtained with test-pieces flexed in the dark.

GRAPHICAL METHOD

In order to apply the graphical method the average number of cycles of flexing (averaged over all 25 test-pieces) required to reach each of the five standard stages of cracking (A to E, B.S.903) were calculated. Five lines were drawn parallel to the X-axis representing each stage of cracking, the displacement of each line up the Y-axis from the origin being proportional to the average number of flexing cycles to each stage of cracking. The mean results for each compound at each stage of cracking were then plotted as described in reference 3. To fit a straight line to each graph, points were found mid-way between stages A and B and between stages D and E and joined by a straight line. The following figures were then read from the intersection of the straight line with the various stages of cracking.

1. Initiation time—intersection with stage A.
2. Initiation and propagation time—intersection with stage E.
3. Propagation time—(2) minus (1).
4. Ratio of propagation time to initiation time—(3) divided by (1).
5. Time to standard stage of cracking—intersection with stage C.

LOGARITHMIC METHOD

The logarithmic value of flex-cracking resistance for each test-piece was found in Table 6 of Newton and Scott[14], and the corresponding results for each lot (A to E) were averaged. The antilogarithms were calculated for comparison with the time to standard stage of cracking obtained by the graphical method.

COMPARISON OF RESULTS

As described above the number of cycles required to cause cracking to proceed to stage C was determined by both the graphical and logarithmic methods.

FLEX-CRACKING RESISTANCE

(STAGE C)

Lot	Graphical kc.	Logarithmic	
		kc.	Log. kc.
A	30.8	30.9	1.49
B	34.5	36.3	1.56
C	30.0	30.9	1.49
D	31.9	33.9	1.53
E	40.0	39.8	1.60

The graphical method also gave the following additional information.

It can, therefore, be concluded that when determining the flex-cracking resistance as defined in B.S.903 (number of cycles to stage C), the graphical and logarithmic methods would appear to be interchangeable, since they give practically the same results.

The graphical method gives, in addition, the relative crack initiation and propagation characteristics. For example, Lots A and E have a similar ratio for propagation to initiation, but E is superior, since its initiation time is longer. Comparing A with B, however, B has slightly poorer initiation characteristics, but is superior in propagation characteristics and the ratio is high. The

Lot	Kc.			
	Initiation	Initiation + propagation	Propagation	Ratio
A	14.0	45.2	31.2	2.22
B	11.0	55.5	44.5	3.28
C	14.8	43.5	28.7	1.93
D	12.8	49	36.2	2.82
E	18.2	60	41.8	2.30

logarithmic method gives no information on these properties.

The graphical method does provide additional information to that obtained from the logarithmic method, and Newton himself was generous enough to recommend the graphical method for international standardization. Until the method is used more widely by other investigators however, it is useful to know that the graphical and logarithmic methods do appear to be interchangeable. One advantage of the logarithmic method is that the accuracy of the logarithmic result can be assessed readily, and it is not a simple matter to assess the accuracy of the results obtained by the graphical method. The importance of this point should not be overstressed however.

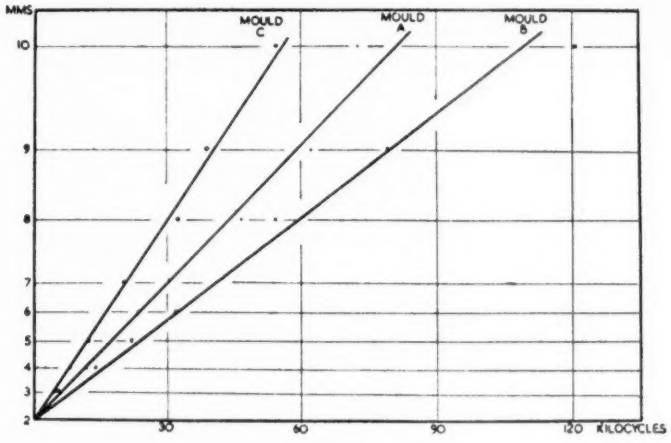


FIG. 4.—Interpretation of crack-growth results by graphical method.

This graphical method can easily be simplified to treat crack-growth results. In this case many of the variations in crack initiation have been removed by the introduction of an initial cut or crack. If an initial crack of 2 mm. is inserted in the test-piece, and the number of kilocycles noted for the crack to grow to 8 mm. in steps of 1 mm. the results can be treated as in Figure 4. In the majority of cases the crack growth up to 8 mm. will be approximately linear, and therefore no adjustment of the ordinate scale is required. As stated earlier in this paper, the author suggests that crack initiation should be measured by the kc. required for an initial crack of 2 mm. to reach 4 mm. and crack growth by the kc. required for the 4 mm. crack to grow to 8 mm.

METHODS OF PRODUCING INITIAL CUT IN CRACK-GROWTH TESTS

The suggestions made for methods and tools to produce the initial cut in crack-growth test-pieces are legion. Buist and Powell[15] showed conclusively that when the incision was made with a round needle it consisted of an irregular star shaped system of tears and suggested the use of a spear-shaped needle so that the initial crack would be orientated along the groove of the test-piece. This suggestion was made at the 1950 Akron meeting of ISO/TC/45, and the American delegation revealed that they had done similar work. The American delegation to ISO/TC/45 later suggested that a chisel tool be considered for international standardization, and this was accepted tentatively by all delegations. The only obvious objection to the chisel, which inserts an initial cut of 2 mm., is the danger that the rubber may be torn by the sides of the chisel, thereby leading to secondary cracks. However, tests carried out so far show that, although this does occur with certain compounds, it is not a serious defect with tread stocks.

Another method of carrying out crack-growth test would be to insert a razor cut along the whole length of the groove, and the crack growth would be measured by following the rate at which the crack grows in depth. This method would remove the difficulties that occur due to secondary cracks starting from the edge of the test-piece. In order to carry out preliminary tests,

modifications were made to the I.C.I. Tear Cutter[16] so that De Mattia test-pieces could be held in a special holder which fitted the base of the tear cutter. By this technique a single cut of known depth can be put in a test-piece along the whole length of the groove.

Previously crack growth and flex-cracking tests have been carried out mainly with tread compounds. There is considerable interest at the present time in crack-growth tests for soling compounds and the British Boot, Shoe and Allied Trades Research Association[17] (S.A.T.R.A.) issued a crack-growth method for resin-rubber soling. S.A.T.R.A. now recommend that the I.S.O. chisel be used to insert the initial crack, and they specify that the initial crack shall not reach either edge of the test-piece after bending and straightening 500,000 times. This illustrates the importance of appreciating that the rate of growth can decrease rapidly after the crack has proceeded to 50–60 per cent of the total width of the test-piece. It is completely wrong to classify materials as satisfactory or unsatisfactory as a result of such a test, because unsatisfactory material may pass the specification and yet have too high an initial crack growth. It would be preferable to specify that the initial crack of 2 mm. should not grow beyond a length of 8 mm. after bending and straightening x times.

The three methods (spear, chisel, and razor) of inserting the initial crack have been used in a study of crack growth using the following compounds:

(*a*) natural-rubber tread without antioxidant (W.8186) (Figure 5).
(*b*) British standard soling mix (W.8187) (Figure 6).
(*c*) hard natural-rubber soling (W.8188) (Figure 7).
(*d*) solid high-styrene soling (W.8189) (Figure 8).
(*e*) microcellular high-styrene soling (W.8196) (Figure 9).
(*f*) microcellular high-styrene soling (W.8197) (Figure 10)
(*g*) natural-rubber sponge soling (W.8195) (Figure 11).

Details of the compounds are given in Appendix I.

The results obtained are illustrated by Figures 5 to 11 in order to demonstrate some of the difficulties.

FIGURE 5

Either of the three methods of inserting the initial crack appear to be satisfactory with a natural-rubber tread, and the crack grows uniformly in depth and across the test-piece from the chisel and spear cuts and uniformly in depth from the razor cut.

FIGURE 6

No serious difficulties are experienced with the British Standard soling compound, and again all three methods of inserting the cut are satisfactory.

FIGURE 7

With the very hard soling mix (85° Shore hardness) neither method is entirely satisfactory. The razor blade technique is completely unsatisfactory for, due to the hardness of the material, the crack does not grow in depth but undercutting occurs (see Figure 12). Even with the chisel and spear cuts, the crack grows unevenly due to the stiffness of the stock. Undercutting occurs when there is a large localized stress vertical to the surface of the rubber, and these conditions apply whenever a very stiff test-piece is used.

FIGURE 8

Exactly the same difficulty is met when a hard solid high-styrene soling is used (87° Shore hardness). In this case the uneven distribution of stress in the region of the chisel and spear cuts leads to a most complicated and confused development of cracking in many planes. The cracking does not proceed in

FIG. 5.

FIG. 6.

depth but is confined almost entirely to the development of undercutting in various planes. As this undercutting proceeds the rate of growth decreases, and in extreme cases, even with continued flexing, the rate of growth appears to drop almost to zero. This undoubtedly gives rise to poor reproducibility of results. Once more the razor blade cut grows entirely in the form of undercutting.

FIGURES 9 AND 10

Two mixings of microcellular high-styrene soling were studied. Once more undercutting occurs with the razor-blade cut. This is clearly shown by the

close up in Figure 13. The crack produced by the chisel and spear grew in a confused manner.

FIGURE 11

The compound studied is a normal natural-rubber sponge soling. The compound is soft but, due to the sponge cells being discrete units, cracking proceeds in an irregular manner in all three test-pieces. There seems to be little

FIG. 7.

FIG. 8.

to choose between any of the three methods of inserting the initial cut when testing sponge compounds of this type.

These results demonstrate clearly that the I.S.O. chisel is satisfactory for normal rubber compounds, but none of the three methods investigated is satisfactory for hard materials, *e.g.*, above 80° Shore. Undercutting occurs with the harder materials, and this is due to the effect of the stiffness of the com-

FIG. 9.

FIG. 10.

pound on the distribution of stress during cracking. This effect is not confined to any one material as undercutting has been found with highly loaded natural-rubber/carbon black soling, a hard resin rubber soling, and also with micro-cellular high-styrene solings.

SUMMARY

The De Mattia test has been chosen for international standardization and work is in progress to establish the test conditions for flex-cracking and crack-growth tests. Cooperative crack-growth tests carried out in nine laboratories have shown that the agreement between laboratories is poor. Various important factors affecting crack growth and flex-cracking are discussed. It is shown that, with the exception of Butyl rubber, the rate of cracking increases with a rise in temperature with natural rubber, Neoprene-GN, GR-S, and Perbunan.

FIG. 11.

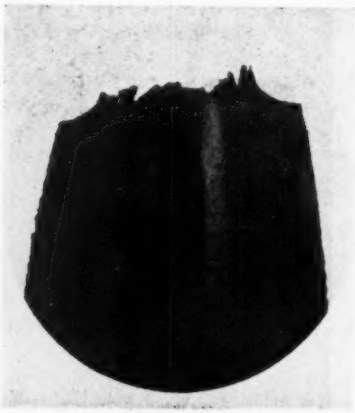


FIG. 12.

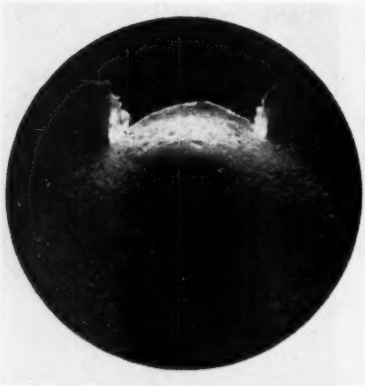


FIG. 13.

GR-S and particularly Neoprene-GN are most sensitive to temperature. Butyl rubber has a low temperature coefficient and is insensitive to increase of temperature over the range 40–100° C.

The mean strain and the dynamic strain imposed on the test-piece have a pronounced effect on the rate of cracking. The factors governing the mean strain and the dynamic strain are the relative setting of the fixed and movable clamps, the amplitude of movement of the moving clamp and the free length of test-piece between the clamps. Present specifications (ASTM D430 and B.S.903) state that the free length of the test-piece should be $3\frac{1}{4}$ inches, and it is shown that if this length is reduced to 3 inches the rate of cracking is much increased. This desirable increase in rate is due to the fact that the 3-inch test-piece is subjected to a higher range of strain and is also returned to zero strain during each cycle. It is also established that small changes in the free-

length of the test-piece between 3⅛ and 3¼ inches produce a larger difference in rate of cracking than do changes between 3- and 3⅛-inch free length of test-piece. The suggestion is made that in future specifications a free length of test-piece of 3 inches should be adopted.

Three essential requirements for a crack-growth test are listed, and it is proposed that measurements should be confined to the earlier stages where the crack grows at a nearly linear rate, and it is suggested that crack initiation should be measured by the kc. required for an initial crack of 2 mm. to reach 4 mm. and crack growth by the kc. required for the 4-mm. crack to grow to 8 mm. An experiment to compare results with test-pieces molded in two multi-cavity molds and test-pieces cut from a molded sheet showed no significant difference between the two methods of molding or the two molds. Nevertheless, the presence of large errors makes interpretation difficult, and it is pointed out that the effects might have been shown significant if a larger number of replicate test-pieces had been used.

Results are given to show that the graphical method of interpreting flex-cracking results developed by Buist and Williams is interchangeable with Newton's logarithmic method. The graphical method has the advantage that it is simpler to apply and in addition extra information is obtained from the results in the form of initiation times and propagation times.

The final section of the paper illustrates the effects produced by the three methods of introducing the initial crack into the test-piece. The initial crack can be produced by (1) a spear-shaped needle, (2) the small chisel recommended for study by ISO/TC/45, or (3) a razor blade. Tests were carried out with the three methods on a natural-rubber tread, three types of solid soling, two types of microcellular high-styrene soling, and a natural-rubber sponge soling. The results demonstrate clearly that the I.S.O. chisel is satisfactory for normal rubber compounds, but none of the methods investigated are satisfactory for hard materials above 80° Shore hardness. With the harder compounds, undercutting occurs and cracking does not proceed in a uniform manner. This difficulty has been found with a highly loaded natural-rubber/carbon black soling, a hard resin-rubber soling, and also with microcellular high-styrene solings. Further work is required before a suitable remedy can be suggested.

ACKNOWLEDGMENT

The author wishes to express his gratitude to his colleague, G. E. Williams, for helpful discussions on various aspects of the work reported in this paper.

REFERENCES

[1] Buist and Williams, *India Rubber World* **124**, 320, 447, 567 (1951).
[2] Newton, *Trans. Inst. Rubber Ind.* **15**, 172 (1939).
[3] Buist and Williams, *Trans. Inst. Rubber Ind.* **27**, 209 (1951).
[4] Somerville, *Ind. Eng. Chem.* **11**, 28 (1936).
[5] Rainier and Gerke, *Ind. Eng. Chem. Anal. Ed.* **7**, 368 (1935).
[6] Carlton and Reinhold, *India Rubber World* **108**, 141 (1943).
[7] Breckley, *Rubber Age* (N. Y.) **53**, 257 (1943).
[8] The Flipper machine used in this work was similar to that described in B.S. 903, Section 26.3.
[9] Cooper, *Ind. Eng. Chem. Anal. Ed.* **2**, 391 (1930); Busse, *Ind. Eng. Chem.* **26**, 1194 (1934); Rainier and Gerke, *Ind. Eng. Chem. Anal. Ed.* **7**, 368 (1935); Cassie, Jones, and Naunton, *Trans. Inst. Rubber Ind.* **12**, 49 (1936); Cadwell *et al.*, *Ind. Eng. Chem. Anal. Ed.* **12**, 19 (1940); Prettyman, *Ind. Eng. Chem.* **36**, 29 (1944).
[10] Holt and Knox, *Rubber Age* (N. Y.) **60**, 689 (1946).
[11] Anon., *India Rubber World* **126**, 5, 655 (1952).
[12] ISO/TC/45 Report on Oxford Meeting, **1951**; Am. Soc. Testing Materials, D-813.
[13] Newton, *Trans. Inst. Rubber Ind.* **15**, 358 (1939).

[14] Newton and Scott, *J. Rubber Research* **16**, 245 (1947).
[15] Buist and Powell, *Trans. Inst. Rubber Ind.* **27**, 49 (1951).
[16] Buist and Kennedy, *India-Rubber J.* **110**, 809 (1946); *J. Sci. Instruments* **23**, 242 (1946).
[17] British Boot, Shoe, and Allied Trades Research Association (SATRA), "Draft memorandum on recent developments in composition materials for shoe soles and heels," 1950.

APPENDIX I

Standard Tread Compound Without Antioxidant

	W.8186
Smoked sheet	100
Zinc oxide	5
MPC black	47.5
Stearic acid	3
Sulfur	3
Mercaptobenzothiazole	0.85

Cure: 45 minutes at 141° C

B.S. Soling Compound Without Antioxidant

	W.8187
Smoked sheet	100
Zinc oxide	4
Stearic acid	3
Di-octylphthalate	3
EPC black	60
Whiting	60
Mercaptobenzothiazole	1
Sulfur	3

Cure: 40 minutes at 153° C

Hard Soling Compound Without Antioxidant

	W.8188
Smoked sheet	100
Stearic acid	4
Zinc oxide	5
MPC black	85
China clay	45
Sulfur	4
Benzothiazolyl disulfide	1.5
Tetramethylthiuram disulfide	0.15
Mineral rubber (MRX)	30

Cure: 6 minutes at 158° C

Solid High–Styrene Soling

	W.8189
Smoked sheet	30
Polysar SS-250	50
Winnofil	80
Turkey red oxide 2GS	1
Yellow oxide 5GS	3
RF Furnace black	0.2
Zinc oxide	5
Stearic acid	1.5
Mineral oil	3
Sulfur	3
Vulcafor-F	1.25

Cure: 30 minutes at 141° C

NATURAL RUBBER SPONGE SOLING

	W.8195
Pale crepe (masticated 30′ cold)	100
Zinc oxide	3
Whiting	50
China clay	50
Petroleum jelly	15
Stearic acid	5
Sulfur	2.5
Tetramethylthiuram monosulfide	0.75
Vulcacel-BN	1.0

Cure: 25 minutes at 141° C

MICROCELLULAR HIGH STYRENE SOLING

		W.8196	W.8197
Crepe	Peptized 10′/100° C	50	50
Polysar SS-250	Peptized 10′/100° C	50	50
Peptizing agent	Peptized 10′/100° C	1.2	1.2
Petroleum jelly		10	—
Stearic acid		4	4
Calcium silicate		60	60
Solka-Floc*		15	15
China clay		30	30
Zinc oxide		4	4
Titanium dioxide		5	5
Vulcafor fast yellow RS		0.025	0.025
Vulcacel-BN		3.5	3.5
Sulfur		2.5	2.5
Vulcafor-DHC		1	1
Paraffin wax		2	2
Coconut oil		1	—
Cumar gum		—	10

Cure: 10 minutes at 141° C

* Heat at 100 C in oven and add hot.

RAPID PLASTOMETRY *

J. R. SCOTT

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

INTRODUCTION

Most of the processes through which rubber stocks have to pass before vulcanization, especially extruding, calendering, and frictioning, depend for successful and regular operation on having stock of the right "plasticity"—to use a convenient word for the whole complex more correctly termed rheological properties. The significance of these properties in processing operations has been fully discussed in a previous paper[1].

There are two distinct purposes for which plasticity measurements might be used. First, a full knowledge of the plastic properties of a stock would make it possible to predict its behavior in any processing operation, thus eliminating much time-wasting trial-and-error and faulty production. This desirable state of affairs is still a long way off, though we must not lose sight of it as the ultimate goal.

The second purpose of plasticity testing is as a control to ensure that successive batches of similar stock will behave sufficiently alike to avoid trouble. It is with this control aspect that this paper deals, and which introduces the need for a rapid test.

Before considering rapid plasticity testing in detail, it is essential to realize clearly what such tests attempt to do and the limitations on what it is possible to do. This is necessary because the plastic behavior of unvulcanized rubbers and stocks is extremely complex. For any one material, the rate of deformation depends on the temperature, the magnitude of the applied force, how long the force has acted, and on the previous history of the material—that is, all treatments involving storage, mechanical working, or subjection to heat. The effects of temperature and magnitude of applied force on the rate of deformation are obvious and well known in a general way, but the influence of previous history and of how long the deforming force acts had not been fully realized until the recent work of Mullins and Whorlow[2]. These effects are especially large in stocks containing reinforcing carbon blacks; Figure 1, relating to a 100:40 natural rubber/MPC black stock tested at 100° C in the shearing-cone plastometer[3] at a shear rate of 1 radian/sec., shows how the stiffness (torque) varies greatly with previous storage or heating of the stock and also with continued shearing during the test.

Apart from this complex manner of deformation under load, there is the equally important property of elastic recovery after the deforming force is removed, and this again depends in a complicated manner on many variables.

In factory practice, however, there is one factor which should simplify matters. In most processing operations the stock is subjected to vigorous mechanical working, either in the machine itself or on a warming-up mill just before it reaches the point where its plastic properties are critical—*i.e.*, the die

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 4, pages 175–189, August 1953.

of the extruder or the nip of the calender. This vigorous working, as recent work[2] has shown, tends to eliminate the effects of the previous history of the stock. However, such history effects will still be important in molding, for which the stock is not vigorously worked immediately beforehand.

The plastic behavior of rubber is thus far too complex to be expressed in terms of measurements of one or two properties. Any really rapid test cannot hope to measure more than one or two properties, and hence the test will be of value only if these properties are closely related to all the others that make up the "plasticity" complex. In general, that is, considering all kinds of rubber stocks, there is no such close relation; this is the reason why, for the present, a

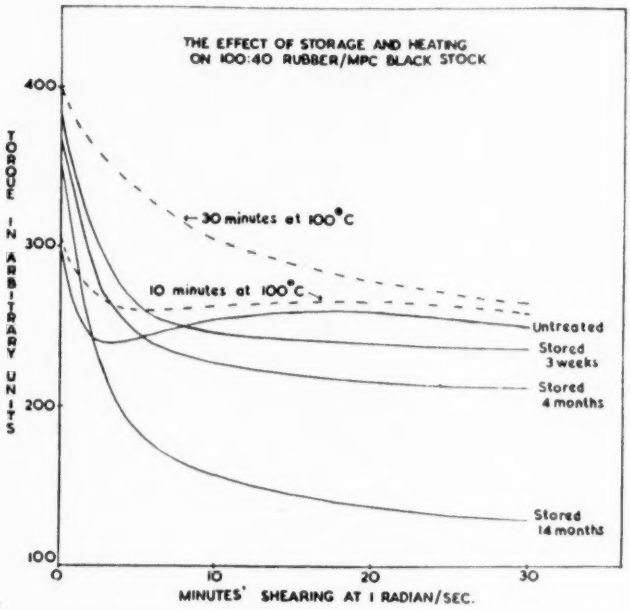


FIG. 1.

simple rapid test cannot hope to predict the processing behavior of new types of stock.

In control testing the problem is easier, because among closely similar materials, such as batches of masticated smoked sheet, or of carbon-black masterbatch, or of finished stock of nominally constant composition, the relation between the various properties involved in plasticity is closer, so that control of any one automatically controls all the others, and tests that give emphasis to different fundamental properties will nevertheless agree, at least within limits.

The important question is: how wide are these limits? The complete answer is not yet known, but the available data show they may be wider than we would like. In Figure 2, the readings of extrusion and rotation (Mooney) instruments are plotted against the corresponding readings on a parallel-plate

compression instrument (Wallace rapid plastometer); the points in each plot are for batches either nominally identical or differing only in milling time. Although there is an obvious relation between compression and extrusion (or Mooney) date, and the scatter of the points is partly due to experimental inaccuracies, the results show that test methods using widely different deformation conditions do not correlate perfectly. Moreover, this example relates to batches processed in the same way; if the processing is changed, *e.g.*, from hot to cold milling or from a roll mill to an internal mixer, then the whole plastic behavior of the rubber may alter.[4] For example, a cold-milled rubber may

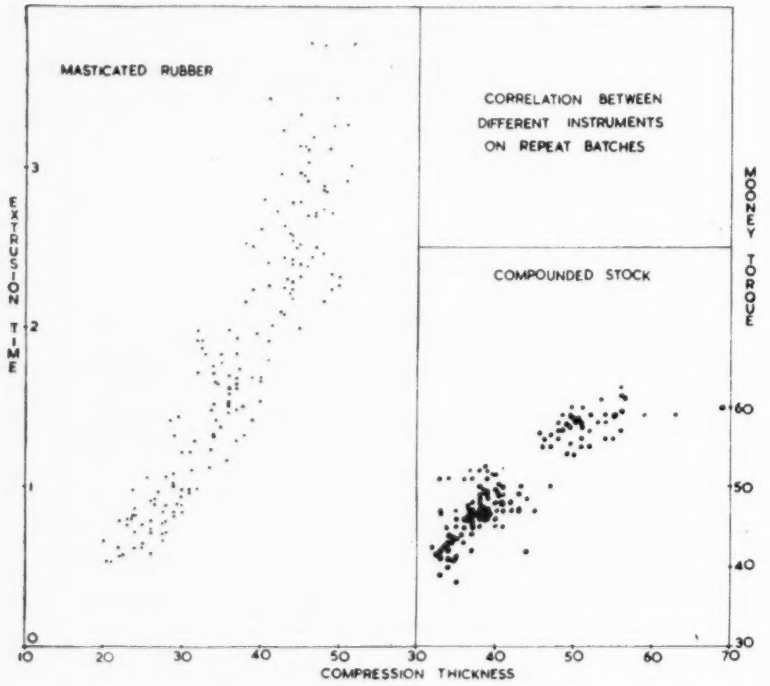


FIG. 2.

appear stiffer than a hot-milled rubber in a test made at a low deformation rate (*e.g.*, Williams plastometer), but softer in a test involving more rapid deformation (*e.g.*, Mooney), and rubbers processed in these different ways can show very different elastic recovery, even though they all give the same Mooney or Williams plasticity reading.

A good beginning has been made in studying the relations between the various plastic properties of unvulcanized rubbers and how these relations are affected by altering the treatment of the rubber,[4] but a definite answer to the question: how useful can a single plasticity measurement be as a control of processing? cannot be given till much more is known, especially as to how much the plastic properties can vary without causing trouble in factory processing.

RAPID PLASTICITY TESTS

It is first necessary to define what is meant by a rapid test. A test may be rapid in either of two ways: (1) by giving the answer quickly, or (2) by enabling a lot of tests to be done in a given time. These are not the same thing; thus a test in which the test-piece has to be preheated for a long time cannot give the answer quickly, but as some test-pieces can be preheating while others are being tested it may still be possible to do a lot of tests in a given time.

Before beginning investigations on rapid plastometry it was important to know which kind of rapid test the industry needs and also certain other relevant information. For this purpose a questionnaire was sent to a number of factories, and it will be of interest to summarize the twenty replies received:—

Which kind of rapid test is wanted?—The replies were not unanimous, but the majority view was that the need is to get the result quickly, so that batches of stock are not held up awaiting a decision as to further processing.

How rapid must the test be?—Statements as to the interval permissible between taking a sample and knowing the result were mostly between 2 and 5 minutes. This incidentally suggests that the instrument should be sufficiently simple and robust to be used in the mill room or in a control laboratory associated with it, since it will not be feasible to transport samples to some distant laboratory.

Uses for a rapid plastometer.—By far the most important purpose visualized for a rapid plastometer was in obtaining the optimum degree of mastication for the next process; next in importance was to obtain a warning of impending scorching. Control of mastication was of interest to all types of manufacturer, whereas avoidance of scorching seemed to concern mainly the larger factories. There was about equal interest in testing masticated rubber and finished mixed stocks; few factories were interested in testing unmasticated rubber.

Who should use the plastometer?—There was a clear distinction between the larger and the smaller manufacturers. The larger ones favored a technical control laboratory making all the tests, whereas the smaller factories were equally divided between those wishing tests to be made by control personnel and those who would leave the use of the instrument to the mill operator, for example to enable an inexperienced mill man to obtain results similar to those obtained by an experienced man.

Thus the need was to design the best possible instrument that would give a result within 2 minutes (if possible) or certainly within 5 minutes, and to be so simple and robust that it could be used in a mill room by an operative not accustomed to scientific measurements.

FACTORS THAT DETERMINE SPEED OF TEST

The time that elapses between taking a sample of stock and getting a plasticity result comprises: (1) time for preparing the test-piece; (2) time for preheating this to the test temperature; (3) time for making the measurement. Whorlow[5] has shown the values of these time elements for plastometers of the following types: parallel-plate compression (Defo[6], Williams, Hoekstra[7]), rotation (Mooney), and extrusion (Dillon[8]); the test conditions for the Williams and Mooney instruments are the British Standard recommendations[9], but as these do not define a Mooney test period, the period agreed by Committee ISO/TC/45 of the International Organization for Standardization[10] was used.

The most striking feature of this analysis is the long time taken by preheating in some of the methods. This is due to the relatively large test-piece used.

Since the temperature must be controlled within fairly close limits, the first step in speeding up the test is to make the test-piece thin so that heat can get into it quickly.

The time for making a test-piece is never more than about one minute; this assumes the use of a mechanical cutter such as the rotary cutter developed for use with the Defo plastometer or the pincers type of cutter devised by Hoekstra.

The test period is longest in the Mooney viscometer; the reason for this is not a very scientific one. It is that the Mooney test is the only one (of those here considered) in which the reading can be seen to change with time under

TABLE 1

Instrument:	Defo	Williams	Mooney	Dillon	Hoekstra
Time (minutes) for:					
Making test-piece	1	1	1	0.5	0.25
Preheating	20	15	1	6	0.17
Testing	0.5	3	4	c.1	0.25

constant shearing conditions (due to thixotropy), and the 4-minute period has been chosen because it suffices to reach a steady reading on masticated rubber, though not with carbon black stocks. The same thixotropic change must occur in extrusion and compression tests, but cannot be detected in the readings, and so is conveniently ignored. Under some conditions the resulting error is negligible; thus, data of Mullins and Whorlow[11] indicate that well masticated raw rubber tested soon after removal from a mill will show very little thixotropic change during the test, though lightly masticated rubber will show more, and carbon black stocks very much more.

CHOICE OF TYPE OF PLASTOMETER

In deciding upon the ideal instrument, it is first necessary to choose between the three basic types: extrusion, rotation, compression.

Extrusion Plastometers

It is difficult to conceive a simple extrusion plastometer which does not use a fairly massive test-piece and thus involve a long preheating period, so that the prospects of a very quick test of the extrusion type seem remote.

Rotation Plastometers

Existing rotation instruments likewise use fairly thick test-pieces (*e.g.*, 0.1 inch in the Mooney viscometer); incidentally, the 1-minute preheating time for this test is not enough to heat the specimen through uniformly (recent American work shows that it needs at least 5 minutes), but this short period is partly compensated by the 4-minute test period.

The idea of using a smaller clearance between the rotor and die in instruments of the Mooney type has not hitherto been tried because of the supposed necessity for grooving the surfaces. However recent evidence[12] that grooving may be unnecessary suggests that the use of smaller clearances between rotor and die, and hence of shorter preheating times, is worth investigating.

Compression Plastometers

In compression instruments the ideal of a thin test-piece can easily be achieved by precompressing it to a small thickness before preheating. This is

one of the most valuable features of the rapid plastometer described by Hoekstra[7]; in this instrument the specimen, a disc 12 mm. diameter and 3–5 mm. thick, is first compressed to 1 mm. thickness and held there for the preheating period of 10 seconds, after which the load is applied and the test proper starts.

One disadvantage of the compression type of plastometer often emphasized is that the rate of deformation produced is very much less than in operations such as extruding, calendering, and frictioning, whereas the rotation and extrusion plastometers come nearer to these high rates. However, in testing masticated raw rubber this disadvantage of the compression instrument is not

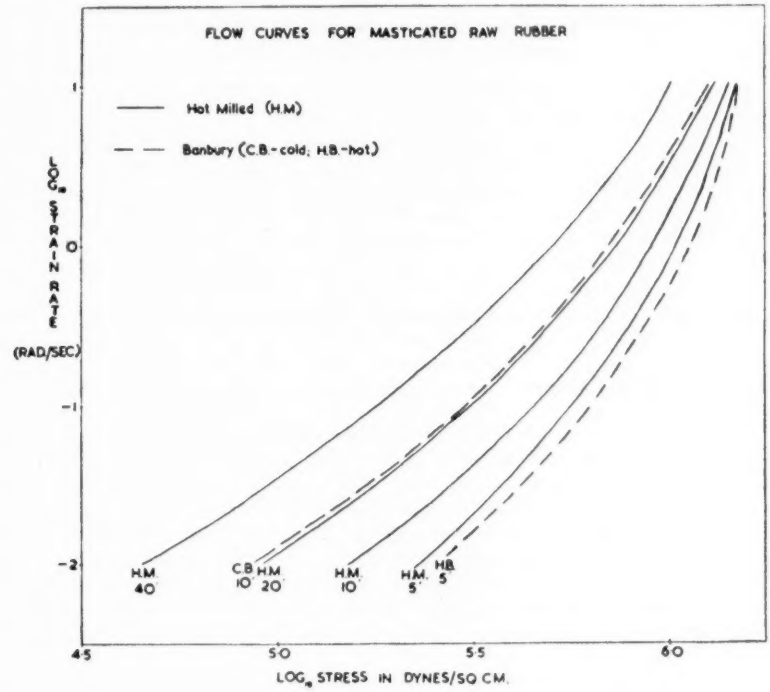


FIG. 3.

so serious as might appear at first sight. Recent experiments show[13] that, provided the conditions of mastication are not radically changed, a test at a low shear rate will put batches in the same order as a test at a much higher rate. Figure 3 shows graphs (on logarithmic scales) of shear strain rate against shear stress for smoked-sheet batches masticated for various times under various conditions; it is clear that tests at 0.01 radian per second would correctly predict the relative behavior of these batches at deformation rates at least 1000 times as great, *i.e.*, 10 radians per second or above. (It will be noted, incidentally, that the curves for Banbury mastication fit into the same series as those for hot mill mastication). This simple state of affairs, however, is not

necessarily found with unmasticated or lightly masticated rubbers or compounded stocks.

The ease with which a thin test-piece can be achieved in a compression plastometer, thus overcoming the preheating problem, led to the adoption of the parallel-plate compression principle as the basis for developing a quick-acting instrument. A further justification is that a compression instrument can be relatively simple and therefore inexpensive. As the remainder of this paper deals exclusively with compression instruments, it is well to emphasize here that such instruments are not considered superior in general to rotation or extrusion instruments, but only in the limited aspects of rapidity and simplicity.

FACTORS AFFECTING THE EFFICIENCY OF A COMPRESSION PLASTOMETER

Having selected compression between parallel surfaces as the basis of the test, the detailed conditions must next be decided, viz., size of compression plates; dimensions of test-piece; release medium (to prevent troublesome sticking of the rubber to the plates); precompression (to what thickness and for how long); compressive load; period of application of this load; and temperature. Much experimental work has been devoted to studying the effects of these variables on the efficiency of the compression test as a means of control in the factory. As a detailed account of most of this work has been published, it is necessary only to indicate the line of approach and the main conclusions[14]. In assessing the efficiency of a plasticity test, three factors have been taken into account.

Discriminating Power

The first factor is how reliably the test gives the information required. The purpose of a routine plasticity test is generally to show whether a batch has received the right amount of working on the mill or in the internal mixer. Hence the test must show up unmistakably any deviation from the correct amount of working. To see how well a test does this, tests must be made on batches worked to different extents, to see how much the results differ. But this is not enough; all instrumental measurements are subject to unavoidable errors, and these may cause a batch that has received more working to appear stiffer than one that has received less working; if this kind of misleading result happens often the test is not very helpful.

Hence in finding how well a test discriminates between a correctly and an incorrectly treated batch, both the difference in reading produced by altering the treatment and the inherent variability of repeat readings on the same batch must be taken into account. This introduces the concept of discriminating power, which in simple language is the ability of the test to distinguish real differences from experimental error; mathematically it is the ratio of the mean squares between samples to the mean squares within samples. (Ref. 14 gives a fuller discussion of this concept of discriminating power.)

Effect of Dimensions of Test-Piece

It is clearly an advantage to have a test that does not require test-pieces of exactly a given size and shape, since this makes their preparation easier and quicker. Hence in assessing the efficiency of a plasticity test, it is essential to

know how much the results are affected by variations in the dimensions of the test-pieces.

Filler Structure

The third factor in assessing efficiency is the effect of the temporary structures that certain fillers, notably carbon blacks, form in rubber stocks, resulting in large differences in measured plasticity according to the previous history of the stock (*cf.* Figure 1). Clearly it will be an advantage to select test conditions that minimize this disturbing influence of carbon structures.

These three criteria—discriminating power, influence of test-piece dimensions, and sensitiveness to carbon black structure—have accordingly been used in the experimental studies, which were made on two series of stocks: (1) five lots of smoked sheet masticated for 0, 10, 20, 30, 40 minutes; (2) five lots of 100:40 rubber/MPC black batch remilled for 5, 10, 15, 20, 25 minutes. The results were unfortunately not all so definite as could be desired, partly because the various factors in the test react on each other and cannot always be varied independently of one another. In particular, it was difficult to get a clear indication as to the conditions that minimize the effects of carbon-black structure. However, useful conclusions were possible as to the best conditions for the test, as follows.

Size of Compression Plates

The first question is the choice between compression plates much larger than the test-piece (as in the Williams plastometer), and plates of which one or both are of similar diameter to the test-piece (as in the Defo and Hoekstra instruments). The experimental results show that by having one or both of the compression plates about equal in diameter to the test-piece (actually 1 cm.), a much better discriminating power is obtained.

The use of one or two small compression plates was also advantageous in making the result less dependent on the size of the test-piece. This confirms a previous investigation[16] on the relative merits of large and small compression plates, which showed also that, although using small plates reduces the effect of varying test-piece size, it does not eliminate this effect, as had been claimed when the use of small plates was first introduced. Little if any advantage is gained by using two small plates rather than one small and one large; indeed, the latter arrangement may be better because it avoids any difficulty in getting the plates concentric.

The choice of the best diameter for the small compression plate is limited by two considerations: (1) To reduce the effect of variations in the size of the test-piece, the diameter of the plate should be much greater than the thickness of the compressed test-piece; (2) The greater the plate diameter, the greater is the compressive load needed, and if this is too great the instrument becomes unwieldy. Assuming a maximum feasible load of 10 kg., the experiments indicated that the plate diameter cannot be greater than about 10 mm., and somewhat less might be advantageous for stiff (*e.g.*, carbon black) stocks.

Dimensions of Test-Piece

The diameter and thickness of the piece are not critical but recent results[17] suggest they do have some influence; in experiments with test-pieces varying in thickness from 2 to 4 mm. and in diameter from 8 to 12 mm., discriminating

power tended to improve as the test-piece was made bigger. However, there is a practical upper limit to the thickness, since a very thick test-piece would take too long to compress to the thickness required for preheating. The size of test-piece adopted in most of our recent work, *i.e.*, 13 mm. diameter and 2.5 mm. thick, seems to be a suitable compromise.

Use of Release Media

To prevent the stock sticking to the compression plates so firmly as to be difficult to remove, it can either be enclosed between two sheets of thin paper or lubricated, *e. g.*, with talc or a silicone fluid. The use of talc or silicone lubricant proved unsatisfactory, because it lubricated the rubber so well that it tended to slip from between the plates when these were first closed together, while talc permitted some sticking to the center of the plates. Moreover, both silicone fluid and talc reduced the discriminating power. The use of thin (cigarette) paper above and below the test-piece is, therefore, the recommended procedure[17].

Precompression and Preheating

The time required to heat a parallel-sided layer of material is proportional to the square of its thickness; hence the less the thickness the better from this point of view. However, if the thickness is too small it becomes difficult to measure its change during the test with sufficient accuracy. These considerations suggested that a thickness of about 1 mm. during the preheating period would be suitable. Using the relation between thickness and time just mentioned, in conjunction with experiments on thicker specimens (1 cm.) preheated for various periods, it appeared that 10–15 seconds should be sufficient to preheat a specimen 1 mm. thick, and tests on a Hoekstra plastometer confirmed that 10 seconds' preheating was enough to give consistent readings. Thus it is concluded that the best procedure is to precompress the test-piece to a thickness of 1 mm. and keep it there for 10 seconds before applying the load.

This precompression appears not to have an important influence on the other criteria of a good plasticity test, though there is evidence that in carbon black stocks precompression may reduce the effect of variations in test-piece dimensions and so improve discriminating power. Precompression might also be expected to break down carbon structures and so lessen their disturbing effect, but it was not possible to demonstrate this experimentally. However, in no sense does precompression appear to be a disadvantage, and its adoption to shorten the preheat period is therefore fully justified.

Compression (Test) Load

The advantage already referred to of working with a large ratio between the diameter of the compression plates and the thickness of the compressed test piece indicates that a large compressive load is desirable. However, practical considerations set an upper limit and 10 kg. has been fixed as a suitable compromise.

Compression Period

Experiments[17] on masticated smoked sheet and carbon black batches, using compression periods from 2 to 32 seconds, show that discriminating power in-

creases with increasing compression period up to about 10 or 20 seconds; also, the effect of variations in test-piece size becomes progressively less as this period is increased. Both these factors thus favor a long compression period. On the other hand, the disturbing effects of carbon black structure are more noticeable with a long compression period[18]. The choice of a compression period therefore has to be a compromise, and it is believed that 15 seconds will in general be satisfactory, though an even shorter period (say, 5 seconds) could give useful results. If such a shorter test were felt desirable, *e.g.*, to avoid carbon structure difficulties, greater care would be necessary in making test-pieces accurately to size.

Temperature of Test

The influence of temperature on discriminating power is complex. For carbon black stocks, 100° C gives better discrimination than a lower temperature such as 70° C, but with masticated smoked sheet the evidence was less definite. Again practical considerations enter, because where steam is available, as it usually is in a factory, 100° C is easily attained without the complications and expense of thermostatic control. A temperature of 100° C has, therefore, been adopted provisionally, although the design of the instrument would permit the use of other heating fluids and, hence, other temperatures.

In concluding this survey of the factors that enter into designing a rapid plasticity test, it must be emphasized that sometimes the optimum conditions differ according to the type of stock being tested. It may thus prove desirable to have an instrument in which certain conditions can be changed to suit different materials. Among the materials to be considered, carbon black stocks are an important yet difficult case, owing largely to the effects of filler structure on the measured plasticity. How serious a disturbing factor this structure is in measurements under factory conditions cannot be said without more experience of the use of rapid plastometers. However, the fact that a rapid test is needed suggests that tests will often be made on stocks taken straight from the mill or internal mixer. In such stocks temporary structures will have been destroyed, and will not reform appreciably if the plasticity test is made without delay.

EXISTING FORMS OF RAPID PLASTOMETER

The first serious attempts to develop rapid instruments were described[19] in 1938. The Defo instrument[20] is quick only in the sense of giving a lot of results in a given time, for a single test takes over 20 minutes.

The Hoekstra instrument achieved much greater speed by using a specimen 1 mm. thick, but in its original form was unwieldy and far from robust—certainly not adapted to factory use. However, it forms the prototype for two more recent instruments, the Wallace rapid plastometer, and the Nedoptifa Plastometer. Only brief particulars of the latter are available.[21]. The Wallace instrument embodies the conditions recommended as a result of the investigations described above; it is shown diagrammatically in cross-section in Figure 4.

The test-piece, between two pieces of thin paper, is inserted between compression plates (A,B), which are, respectively, 10 and 11 mm. in diameter, the former being the critical dimension. The plates form part of hollow chambers through which steam at 100° C is circulated. Plate A is attached to bridge C; moving a handle (not shown) at the base of the instrument depresses the toggles

E which, acting through the rods D and the bridge, pull the plate A down on to the test-piece, which is thus subjected to a considerable force by the springs L. This force effects the precompression, which automatically stops when the test-piece is reduced to 1 mm. thick; precompression is usually complete in 1–2 seconds. Moving the handle also starts a timing device which at the end of 10 seconds (the preheating period) applies the compression load of 10 kg. to the test-piece by the following mechanism. The 10-kg. load, applied upwards to

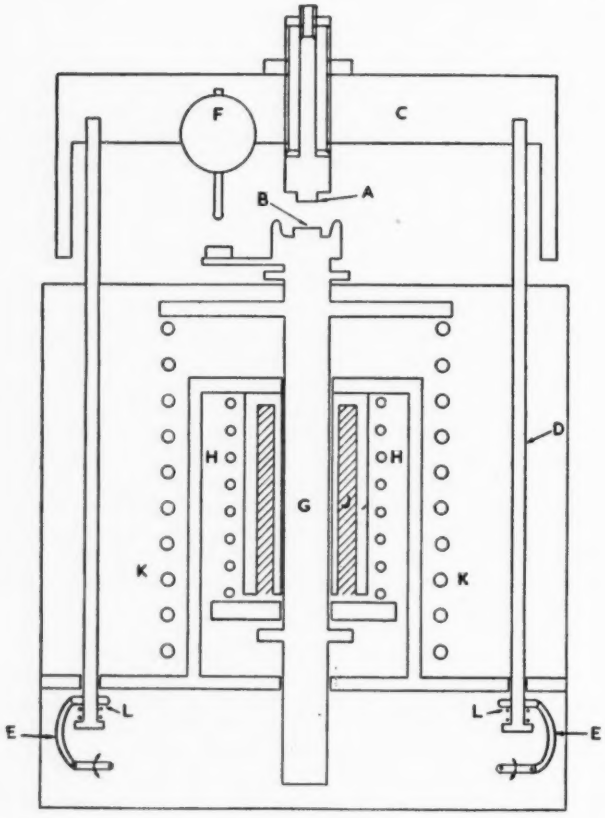


Fig. 4.

the lower plate (B) through rod G, is furnished by the spring K. This spring is normally counterbalanced by a stronger spring H acting downwards; at the end of the 10-second period, spring H is put out of action by the electromagnet J. After K has acted for 15 seconds to compress the test-piece, the electromagnet is automatically switched off, and this spring ceases to act. A non-return mechanism on the dial-gauge F holds the reading at the value reached after 15 seconds' compression.

The handle is finally returned to its original position, thus raising the bridge for the removal of the test-piece and insertion of the next one and also returning the dial gauge to the zero position.

Adjustments are provided for (1) making the precompressed thickness of the test-piece (exclusive of the papers) exactly 1 mm., (2) setting the dial gauge to indicate the thickness of the test-piece correctly. The 10-mm. diameter upper platen can be replaced by a smaller one (7 mm. diameter) for tests on very stiff stocks.

For cutting test-pieces, a pincer type cutter, which will take sheets of rubber up to ½ inch thick, has been designed[22]. A single movement of the handle produces two successive actions: (1) a cylindrical flat-ended plunger 13 mm. diameter compresses a portion of the sheet to 2.5 mm. thick; (2) a hollow cylindrical cutter sliding over the plunger cuts out this compressed portion, giving a disc 13 mm. diameter and 2.5 mm. thick (elastic recovery may, of course, subsequently alter these dimensions, but this does not affect the test result).

There is not yet sufficient experience with these new rapid plastometers to judge finally their practical value. As both instruments are of the parallel-plate compression type, they will have the limitations inherent in this type, as indicated earlier. However, the continued extensive use of compression plastometers shows that the readings are useful in controlling factory processes. Hence the criterion for judging the new instruments is rather the speed of operation and the reliability of results.

The Wallace rapid plastometer has been studied both in the laboratory and, thanks to the Dunlop Rubber Co., Ltd., as a control instrument in the factory. It is not possible yet to publish the full results, but the relevant conclusions are summarized below.

(1) As regards speed and simplicity of operation, experience confirms the advantages expected of the new instrument. In the factory trials very little tuition was needed to make the operators proficient in using the instrument, and little supervision was needed during the trial. The general comment of the operators was very favorable, and the special cutting device made test-piece preparation easy.

(2) Variable results have been observed with some stocks containing crumb, presumably because the thickness of the compressed test-piece is comparable with the size of the crumb particles. Caution is, therefore, needed in applying the Wallace plastometer to crumb stocks.

(3) For any given type of rubber, *e.g.*, masticated smoked sheet, a carbon black master-batch, or a mixed stock of given formula, the readings of the Wallace instrument bear a simple relation to those of the other instruments studied (Williams, Mooney and extrusion plastometers). The Wallace readings plotted against those of the other instrument lie roughly along a straight or curved line, the scatter of the points about the line being largely due to the reading errors inherent in each instrument. However, the line expressing the relationship between the Wallace and the other instrument is not the same for different types of rubber or stock, so that there is no simple conversion table or graph of universal applicability.

(4) In the laboratory and factory trials, special attention was paid to the reproducibility of readings and the discriminating power of the instruments, that is, their ability to distinguish real differences between rubbers from experimental error, as discussed earlier in this paper. Figures for reproducibility are not so immediately helpful because a given difference (actual or percentage)

in reading does not represent the same difference in plasticity with all instruments. Hence the discriminating power is the better criterion of performance. Comparisons of the Wallace rapid plastometer and the standard Williams plastometer, using masticated smoked sheet and carbon-black master batches, have given variable indications as to their relative merits, but generally the Williams instrument appeared to discriminate between batches milled to different extents rather better than the Wallace; this conclusion, however, applies when all tests on one instrument are made by the same operator, and there is evidence that Williams readings are more influenced by change of operator, which would thus reduce its discriminating power.

The Mooney viscometer gave better discrimination than the Wallace instrument on mixed stocks, provided there was no change of operator, but again the operator effect influences the comparison because Mooney readings were affected by change of operator, whereas Wallace readings were not. The extrusion (Griffiths) plastometer had poorer discrimination than the Wallace for masticated rubbers, even in tests by the same operators, and it showed the further disadvantage of being influenced by change of operator.

Taking the results as a whole, the Wallace rapid plastometer, under normal working conditions, seems likely to prove as reliable as existing instruments in checking the correctness of mastication and the uniformity of repeat batches.

SUMMARY

The uses of plasticity tests, especially rapid simple tests, are discussed, with particular reference to the limitations imposed by the complex plastic behavior of unvulcanized rubbers and stocks, leading to the conclusion that simple tests are likely to be of use only for routine control of repeat, nominally identical batches. A summary is given of information collected from the industry to show under what conditions a plasticity test is required to be used in factory control. The *efficiency* of a plasticity test is defined, and a discussion given on how the type of instrument (rotation, extrusion or compression) and the conditions of a compression test affect both efficiency and rapidity, thus showing what conditions furnish the best form of test. It is concluded that the parallel-plate compression test is the most suitable, provided the test-piece is precompressed to a small thickness so that it can be quickly heated to the test temperature before applying the load; other factors considered are the size of compression plates and of test-piece, use of release medium (*e.g.*, thin paper), degree of precompression, preheat period, load, compression period, and temperature. Existing rapid plastometers are described, including full details of the new Wallace modification of the Hoekstra instrument, which embodies the recommended conditions of test.

ACKNOWLEDGMENT

The author wishes to thank the Council of the Research Association of British Rubber Manufacturers for permission to publish this paper, based on work carried out in the Association's laboratories.

REFERENCES

[1] Scott, *Trans. Inst. Rubber Ind.* **20**, 8, (1944).
[2] Mullins and Whorlow, *Trans. Inst. Rubber Ind.* **27**, 55 (1951).
[3] Piper and Scott, *J. Sci. Instruments* **22**, 206 (1945).
[4] Piper and Scott, *J. Rubber Research* **16**, 151 (1947); **17**, 135 (1948).

[5] Whorlow, *J. Rubber Research* **20**, 71 (1951), Table 1.
[6] Odenwald and Baader, *Proc. Rubber Technol. Conf. London*, **1938**, p. 347.
[7] Hoekstra, *Proc. Rubber Technol. Conf. London*, **1938**, p. 362.
[8] Dillon and Johnston, *Physics* **4**, 225 (1933).
[9] British Standards Institution, B.S. 1673, "Methods of Testing Unvulcanized Rubber", Part III, Physical Tests.
[10] Scott, *Trans. Inst. Rubber Ind.* **28**, 249 (1952).
[11] Mullins and Whorlow, *Trans. Inst. Rubber Ind.* **27**, Figs. 1 and 8 (1951).
[12] Braber, *India-Rubber J.* **122**, 715 (1952); Decker and Roth, unpublished experiments.
[13] Whorlow, R. W., unpublished experiments.
[14] Except where otherwise shown, these are taken from Whorlow, *J. Rubber Research* **20**, 71 (1951).
[15] Newton, Scott, and Whorlow, *Proc. Intern. Rheol. Congr.* **1948**, II-204, III-61.
[16] Scott, *J. Rubber Research* **17**, 109 (1948).
[17] Herne, H., Hine, D. J., and Wright, M., unpublished experiments.
[18] Whorlow, *J. Rubber Research* **20**, 71 (1951).
[19] Odenwald and Baader, *Proc. Rubber Technol. Conf. London*, **1938**, p. 347; Whorlow, *J. Rubber Research* **20**, 71 (1951).
[20] Odenwald and Baader, *Proc. Rubber Technol. Conf. London*, **1938**, p. 347; Whorlow, *J. Rubber Research* **18**, 51 (1949).
[21] Soden, "Rubber Technology", Buttersworth, London, **1951**, p. 96.
[22] This cutter was designed by Messrs. H. W. Wallace.

SELF-CLOSING GRIPS FOR RUBBER *

A. J. STUBBS

RESEARCH INSTRUMENT SECTION, DUNLOP RESEARCH CENTRE, DUNLOP RUBBER CO., FORT DUNLOP, BIRMINGHAM, ENGLAND

The provision of satisfactory grips for holding dumb-bell specimens in tensile testing machines has always presented a number of difficulties. Several styles of self-closing grips are available, but none has been regarded as entirely satisfactory. Thus, the cam type is clumsy and often fails to hold the test-piece at very high extension or when the surface of the rubber is covered with a wax bloom, as sometimes happens. Another type, the bar grip, illustrated in

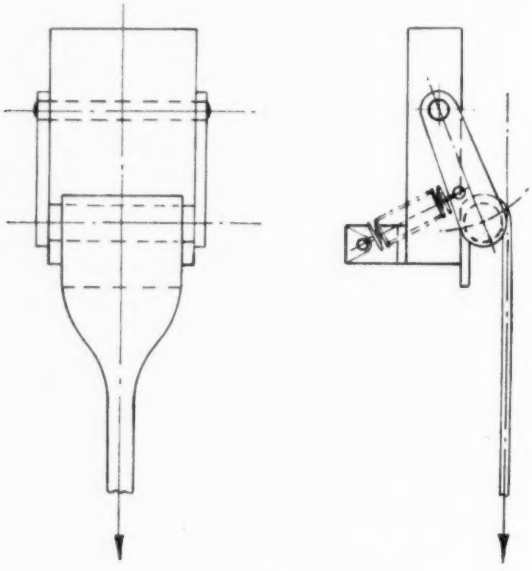


FIG. 1.

Figure 1, has very much better holding power, but requires the specimen to have undersirably long end tabs.

The wedge grip used in metal testing has been taken as a basis for the development of a new design, which is shown in Figure 2, but instead of using

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 4, pages 215–218, August 1953.

plane metal faces for the wedge surfaces, it will be seen that rollers have been introduced in order to reduce the friction and to make the unlocking of the grip easier.

These rollers A are made from $\frac{3}{16}$-inch diameter silver steel rod, and they are constrained in slots cut in part B which are inclined at an angle to each other to produce a wedging action when the rollers are moved up the slots.

The mechanism for moving the rollers in this manner consists of horizontal slots cut in the outer slidable member C, so that the two rollers located in both types of slot are always level with each other. The rollers are separated for insertion of the test-piece by pressing member C downwards (in the lower grip as shown) against the compression spring D. Slight projections E are provided on which finger and thumb can rest to effect this movement.

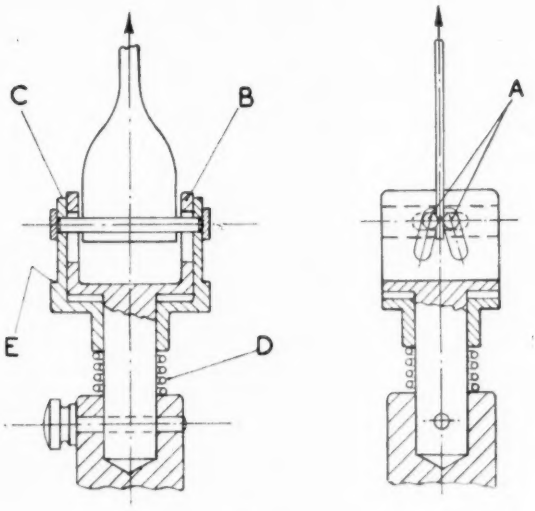


FIG. 2.

The spring exerts just sufficient force, when the finger pressure is removed, to press the rollers against either side of the specimen. The movement of the specimen which takes place in the direction of the tensile load as soon as it is applied draws the rollers further along the inclined slots to produce a tighter grip. The gripping force is thus automatically increased with the tension.

To release the ends of the broken test-piece, all that is needed is further application of the finger pressure at projections E.

This design of grip has been exhaustively tested for several years. It has been found to hold every kind of rubber tested until the specimen has broken in the test length, irrespective of the extension or nature of the surface, and without damage to the ends of the specimen. Accurate positioning of the test-piece is easily and rapidly accomplished, and for this reason the grips have proved particularly valuable for testing at elevated temperatures where simple manipulation is desirable to avoid risk of burns to the operator.

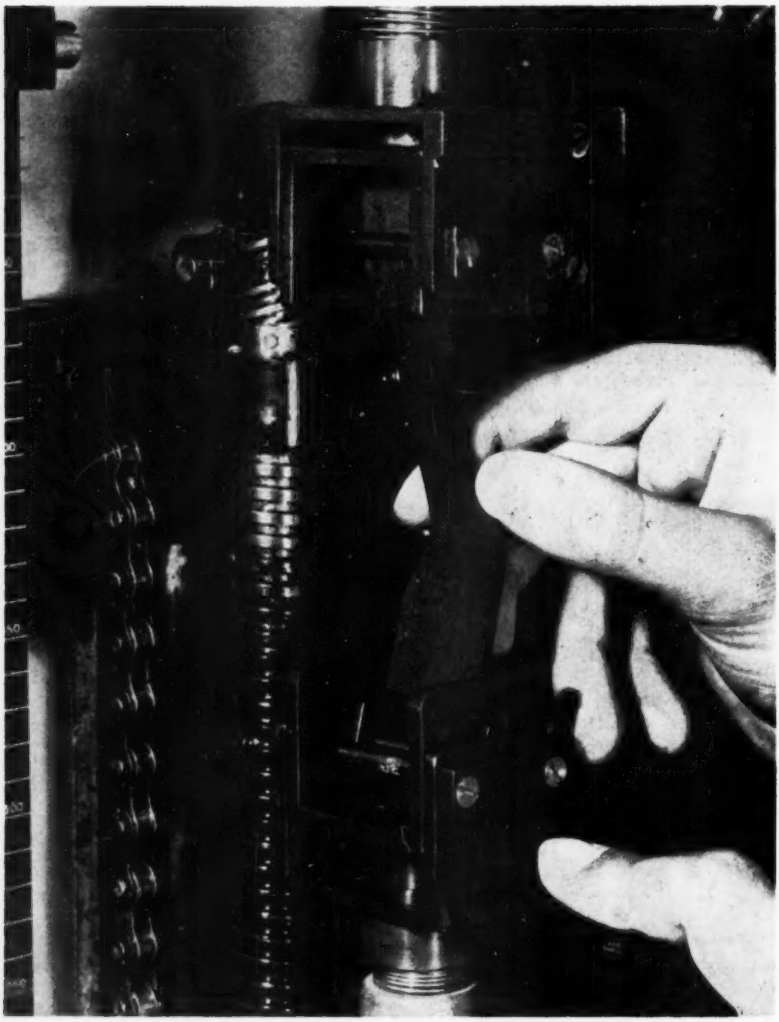


FIG. 3.—Photograph showing insertion of test-piece in grips.

ACKNOWLEDGMENT

Acknowledgment is made to G. Gavin for the method, and to the Dunlop Rubber Company Limited for permission to publish this note.

A STUDY OF THE GOODRICH FLEXOMETER WITH SYNTHETIC POLYMER COMPOUNDS *

B. G. LABBE

GOVERNMENT LABORATORIES, UNIVERSITY OF AKRON, AKRON, OHIO

Published articles relating to the effect of varying the test conditions for the Goodrich flexometer were based on tests with natural-rubber compounds. The original article by Lessig[1] describes the apparatus, method of operation, and type of data obtained. The paper by Mackay, Gardner, and Anderson[2] provides data showing the effect on temperature rise of altering the frequency, applied load, and the deflection.

The purpose of this report is to show similar type of data for compounds of six synthetic polymers in addition to natural rubber, to obtain a comparison of the polymers under varying test conditions, and to indicate a means of adjusting the test conditions so that better reproducibility can be obtained among the various laboratories.

The reputation of lack of reproducibility of data from the Goodrich flexometer should be attributed less to imperfections in the apparatus itself than to lack of proper care in the adjustment of the equipment, improper preparation of test samples, and the ready acceptance of the results for comparative purposes without data to show the effect on the results, caused by adjustments that are not precise.

PROCEDURE

In order to cover the synthetic elastomer field rather comprehensively, the following polymers were selected for testing:

1. Natural rubber
2. GR-S-1000 (X-603)
3. GR-S-1500 (X-624)
4. Polybutadiene (122° F) (XP-155)
5. Polybutadiene (41° F) (XP-150)
6. 80/10/10 BD/I/S (XP-212)
7. Sodium-catalyzed 87.5/12.5 BD/S

The following compounding recipes were utilized:

	Natural rubber	GR-S-1000 122° F	GR-S-1500 41° F	Poly BD 122° F	Poly BD 41° F	BD/I/S 80/10/10	Na-BD/S 75/25
Polymer	100	100	100	100	100	100	100
EPC black	40	40	40	40	40	40	40
Zinc oxide	5	5	5	5	5	5	5
Sulfur	3	2	2	2	2	2	2
Altax		1.75	3	3	3	3	1.25
Captax	0.5						
Stearic acid	2.0		1.5	1.5	1.5	1.5	3.0
PBNA	1.5						

* Reprinted from the *India Rubber World*, Vol. 128, No. 2, pages 193-198, May 1953. The work is a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

Stress-strain data were obtained on vulcanizates cured for 25, 50, 75, 100, and 150 minutes at 292° F. Optimum cures were selected from the modulus *vs.* time-of-cure curves. The hysteresis tests were conducted on optimum cured and 30-minute overcured samples. For natural rubber, three cures (25, 45, and 65 minutes) were evaluated because the optimum cure for this compound is usually high on the temperature rise *vs.* time-of-cure curve.

The effect of loading during these tests with the Goodrich flexometer was studied by decreasing the load from the standard 143 to 115 and 90 lb./sq. in. Because most laboratories test at 212° and at 100° F, variations in applied load and deflection were made at each of these temperatures. Under standard conditions of load and deflection, tests were also made at 158° F.

The normal frequency of 1800 flexures a minute was decreased to 1,500, 1,200, and 980 f.p.m., while the deflection of 17.5 per cent, on the one-inch sample was varied by testing also at deflections of 10 and 25 per cent.

Since the Government Laboratory standard procedure for determining temperature rise is a 30-minute test, all tests in this program were run for a minimum of 30 minutes, except for those made with 25 per cent deflection, in which instance a 10-minute test was made. If the temperature rise between the 20- and 30-minute readings was greater than 2° F, the test was continued until the rise reached equilibrium (*i.e.*, temperature rise of 2° F, or less during a period of 10 minutes). At 100° F, most test-specimens reach equilibrium temperature in 10 to 15 minutes.

DISCUSSION

The effects of the several variables are individually discussed. Hysteresis temperature rise values obtained at overcures are used for graphical presentation of the data since the temperature rise for the optimum cure, selected from the 300 per cent modulus values, usually falls on the steep part of the hysteresis *vs.* time-of-cure curves.

EFFECT OF TEST TEMPERATURE

From the data in Table 1 and the plotted values of the overcures in Figure 1, it appears that the temperature rise of the synthetic polymer compounds tested *vs.* the temperature is a straight-line function, within the limits tested. Of the six synthetic compounds, the temperature rise values of three, at 100, 158, and 212° F, describe straight lines; while for the other three compounds the data in Table 1 indicate a break in the line at 158° F. From a practical viewpoint, the reproducibility of data from the hysterimeter is definitely not better than 2° F. Since by changing the 158° F values by 2° F or less, plotted values for the synthetic polymers fall on straight lines, it appears reasonable to assume that all synthetic polymer compounds would do likewise. The curve for the overcured natural-rubber compound decreased in hysteresis, as the temperature of test was increased from 100 to 158° F, and then remained constant. Hysteresis data for the stocks of natural rubber cured at 25 and 45 minutes show that the effect of the test temperature on the heat rise is not the same for the three cures. With the synthetic, however, the temperature rise for the different cures was straight-line functions (curves not shown) of the test temperatures, within the limits used, but the slopes were not necessarily similar for the different cures of the same polymer.

Straight lines, in Figure 1, plotted from the temperature rise values for the overcures *vs.* increased testing temperature were essentially parallel for the

TABLE 1

EFFECT OF TESTING TEMPERATURES

(Load, 143 lb./sq. in.; throw, 17.5%; frequency, 1800 f.p.m.)

Test temp. (° F)	Min. cured at 292° F	Shore-A hardness	Initial comp. (%)			30-min. temp. rise (° F)			Set (%)		
			100	158	212	100	158	212	100	158	212
Natural rubber*	25	52	25.3	27.1	25.1	57	57	63	11.8	29.0	†42.4
	45	56	20.9	21.8	20.1	42	35	39	4.4	12.3	37.0
	65	59	20.7	21.0	18.6	41	33	33	4.6	8.5	22.3
GR-S-1000	65	63	20.5	21.8	20.7	82	65	55	8.0	11.3	15.4
	95	64	17.9	18.9	18.8	71	58	46	5.0	6.0	8.8
GR-S-1500	55	61	18.6	18.4	19.0	65	56	45	5.3	8.9	14.2
	85	63	16.2	17.0	16.5	58	46	39	2.4	4.6	7.4
Polybutadiene (122° F)	50	58	23.6	21.8	21.0	63	53	48	6.0	11.8	16.5
	80	60	21.6	21.0	17.3	65	52	40	4.5	7.5	9.5
(41° F)	50	64	15.1	14.9	13.6	60	49	39	2.7	5.9	8.6
	80	65	14.8	14.8	15.1	54	47	37	2.8	3.9	6.7
BD/I/S 80/10/10	80	62	15.4	17.6	15.9	56	50	38	2.6	4.5	7.1
	100	63	15.4	16.5	16.1	57	47	38	2.3	3.3	5.1
BD/S 75/25 (Na-catalyzed)	55	59	24.6	25.7	25.0	69	53	40	8.2	12.3	19.3
	85	61	21.7	21.6	20.0	55	43	29	4.6	6.0	11.2

* Cured at 280° F.
† Test exceeded 30 minutes.

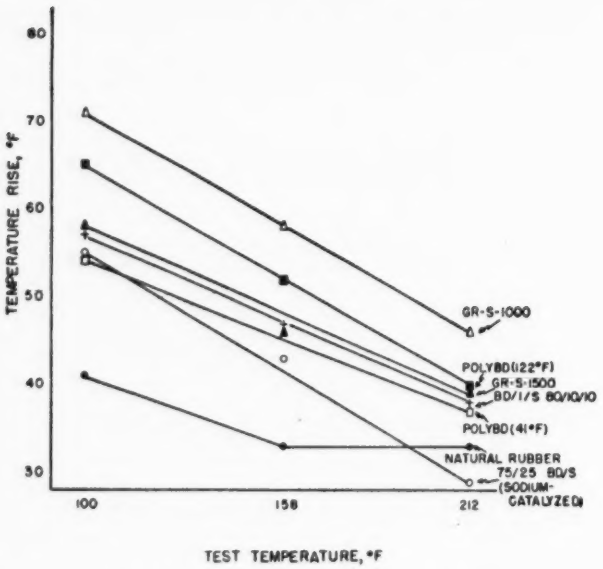


FIG. 1.—Effect of temperature on temperature rise.

cured stocks of GR-S-1000, 122° F polybutadiene, and the sodium-catalyzed polymer. The lines representing temperature rise for the stocks of the overcures of GR-S-1500, 41° F polybutadiene, and the butadiene/isoprene/styrene polymer are approximately parallel, but the maximum difference of temperature rise of about 18° between 100 and 212° F, for the stocks of these three polymers

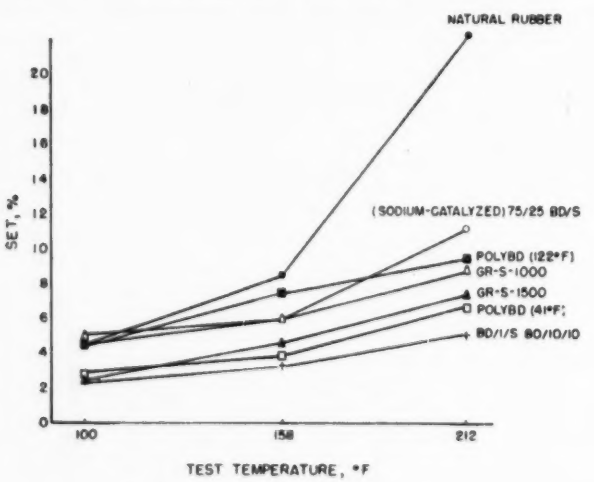


FIG. 2.—Effect of temperature on set values.

is less than the rise of about 25° F for the other three synthetic polymer compounds at the overcure. As the state of cure, as has been shown, may or may not affect the slope of the curves, these differences in slopes are not considered representative of the polymers, but merely fortuitous. These limited test results, however, do raise the question as to the validity of interpreting them to show temperature rise in tires at much higher operating temperatures.

The set values increased with increase in testing temperature, but not in direct proportion to the temperature (Figure 2). Generally, the increase in set values between 158 and 212° F was greater than that between 100 and 158° F, but the state of cure, as well as the type of polymer, seems to affect the change of set with increase of temperature within the range shown. This raises some question as to the desirability of comparing hysteresis properties at equal set values, since these latter may change in a variable manner with increases in temperature depending on the state of cure.

An error of 10° F in testing temperature would cause an error of about 2° F in temperature rise when vulcanizates of synthetic rubber compounds are being tested.

EFFECT OF FREQUENCY

The effect of varying the frequency of strokes at a testing temperature of 212° F is shown by the data in Table 2 and illustrated by the plots in Figures 3 and 4. A decrease of frequency causes a decrease in temperature rise values. The temperature rise is essentially a straight-line function of the frequency, within the limits tested. The limited data shown in Table 2 indicate that with increase of cure, the hysteresis increase with increases in frequency becomes less. That is, the slope of the curve becomes less. Therefore any comparison of the rate of change with frequency is dependent more on the state of cure than on the type of polymer. The temperature rise of natural rubber and the five synthetic polymer compounds increased by 18° to 20° F, over the range in frequency of 980 to 1800 flexures a minute, *i.e.*, a rate of about 2° F per 100 f.p.m. for the overcures. The rise in the case of the sodium copolymer compound was about 1.5° F per 100 f.p.m.

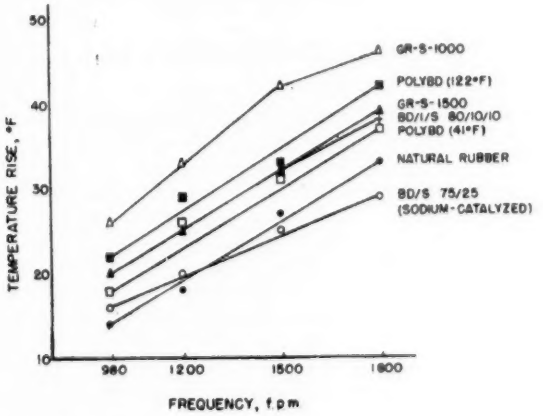


FIG. 3.—Effect of frequency on temperature rise (test temperature 212° F).

TABLE 2

EFFECT OF FREQUENCY

(Load, 143 lb./sq. in.; test temp., 212° F; throw, 17.5%)

Frequency (flexures per min.)	Min. cured at 292° F	Shore-A hardness	Initial comp. (%)				30-min. temp. rise (° F)				Set (%)			
			980	1200	1500	1800	980	1200	1500	1800	980	1200	1500	1800
Natural rubber*	25	53	27.2	26.1	22.9	25.1	29	39	57	63	†27.6	†33.3	—	†42.4
	45	57	21.7	21.5	21.7	20.1	16	22	32	39	14.3	16.4	23.1	†37.0
	65	60	20.5	19.9	19.4	18.6	14	18	27	33	11.9	11.7	13.1	22.3
GR-S-1000	65	63	22.6	22.3	22.0	20.7	28	37	47	55	10.0	12.2	13.5	15.4
	95	65	19.4	19.4	19.4	18.8	26	33	42	46	6.5	7.6	9.0	8.8
GR-S-1500	55	63	18.0	18.5	18.8	19.0	24	30	38	45	7.8	9.7	12.0	14.2
	85	64	16.0	15.7	16.0	16.5	20	25	32	39	4.5	4.8	5.9	7.4
Polybutadiene (122° F)	50	61	21.0	21.8	21.1	21.0	24	31	40	48	11.9	13.4	15.0	16.5
	80	64	19.3	20.4	18.8	17.3	22	29	33	40	6.9	8.6	9.4	9.5
(41° F)	50	65	14.7	14.8	14.9	13.6	22	28	32	39	6.2	6.5	8.6	8.6
	80	67	13.4	13.6	12.7	15.1	18	26	31	37	4.2	4.3	4.6	6.7
BD/I/S 80/10/10	80	64	15.7	14.4	16.3	15.9	19	27	33	38	4.9	5.6	6.3	7.1
	100	65	16.5	15.5	16.3	16.1	20	25	32	38	3.7	4.3	4.7	5.1
BD/S 75/15 (Na-catalyzed)	55	59	25.4	23.7	25.0	25.0	25	29	37	40	14.9	16.2	17.9	19.3
	85	61	22.8	21.8	22.2	20.0	16	20	25	29	8.1	9.3	10.2	11.2

* Cured at 280° F.
† Test exceeded 30 minutes.

As compounded, the natural-rubber stocks increased in set markedly with increase in frequency. From the data in Table 2, it can be seen that the synthetic polymers at either cure increased in set linearly with the frequency, and the slope decreased with an increase in state of cure.

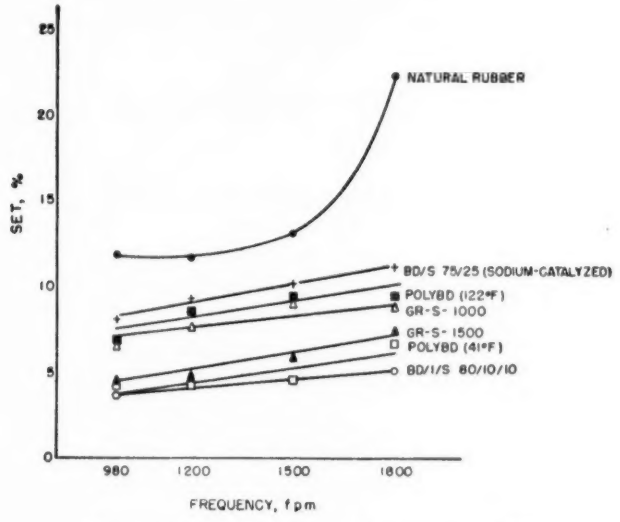


FIG. 4.—Effect of frequency on set (temperature, 212° F).

For the natural rubber compound at the overcure shown in Figure 3 the change in set values is small (1.2 per cent) between 980 and 1500 f.p.m.; but, from 1500 to 1800 f.p.m. the set increased by 9.2 percentage units.

EFFECT OF DEFLECTION

TEST TEMPERATURE, 212° F

The effect of throw or deflection on the hysteresis-temperature rise of the test-specimen during the period of cyclic compression was investigated at both 100 and 212° F. The data obtained at a testing temperature of 212° F are shown in Table 3. When the deflection was increased to 25 per cent of the original height of the specimen (instead of the standard, 17.5 per cent), the samples failed before the end of the 30-minute period because of the severity of the stroke. To obtain a comparison of hysteresis-temperature rise values of the various compounds, it was therefore necessary to use the data obtained for the 10-minute test at 212° F (Figure 5). The set values are for specimens tested at 30 minutes and consequently do not coincide with the temperature rise values.

An increase in the deflection or throw causes an increase in hysteresis greater than a first-order response for the states of cure examined (Figure 5). Decrease in the state of cure caused a greater increase in hysteresis with increase in the per cent deflection. At 17.5 per cent throw, an error of one percentage

TABLE 3

EFFECT OF VARYING DEFLECTION

(Load, 143 lb./sq. in.; test temperature, 212° F; frequency, 1800 f.p.m.)

	Min. cured at 292° F	Deflection (%) Shore-A hardness	Initial comp. (%)			10-min. temp. rise (° F)			Set (%)		
			10.0	17.5	25	10.0	17.5	25	10.0	17.5	25
Natural rubber*	25	52	27.9	25.1	27.8	10	32	106	23.5	—	—
	45	57	22.0	20.1	20.7	6	23	69	11.9	—	—
	65	59	19.7	18.6	20.3	3	30	63	9.2	—	—
GR-S-1000	65	63	21.0	20.7	22.7	16	47	101	5.9	15.4	—
	95	65	19.5	18.8	20.4	14	37	87	3.9	8.8	—
GR-S-1500	55	62	18.4	19.0	18.9	13	38	78	5.7	14.2	—
	85	64	16.1	16.5	15.6	10	35	64	3.2	7.4	—
Polybutadiene (122° F)	50	59	20.6	21.0	20.4	11	40	77	8.4	16.5	—
	80	61	19.6	17.3	19.1	11	34	72	5.4	9.5	—
(41° F)	50	65	15.3	13.6	13.8	10	36	54	4.5	8.6	—
	80	66	13.5	15.1	13.1	10	34	†	2.4	6.7	—
BD/I/S 80/10/10	80	62	18.7	15.9	15.1	11	33	68	3.2	7.1	—
	100	62	16.3	16.1	15.1	11	35	54	2.9	5.1	—
BD/S 75/25 (Na-catalyzed)	55	61	25.9	25.0	25.6	11	34	70	10.2	19.3	—
	85	62	21.4	20.0	21.8	7	25	59	5.6	11.2	—

* Cured at 280° F.

† The specimens slipped from between the anvils at four and seven minutes; the temperature rise values were 26 and 31° F, respectively.

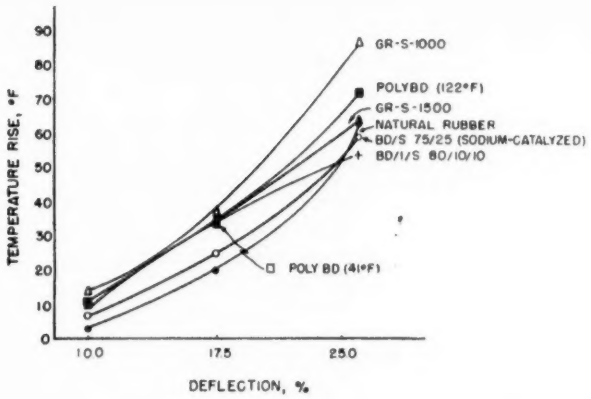


FIG. 5.—Effect of deflection on temperature rise (test temperature, 212° F 10-minute test).

unit in deflection will cause a difference of about 3° to 4° F in the temperature rise at a test temperature of 212° F at the cures shown.

TEST TEMPERATURE, 100° F

At a test temperature of 100° F, similar variations in percentage deflection were made; 30-minute temperature rise values were obtained for five of the seven polymer compounds (data in Table 4, plotted in Figure 6). With an increase in deflection, the rise is greater in 30 minutes at 100° F than in 10 minutes at 212° F, and an error of one percentage unit in deflection will cause

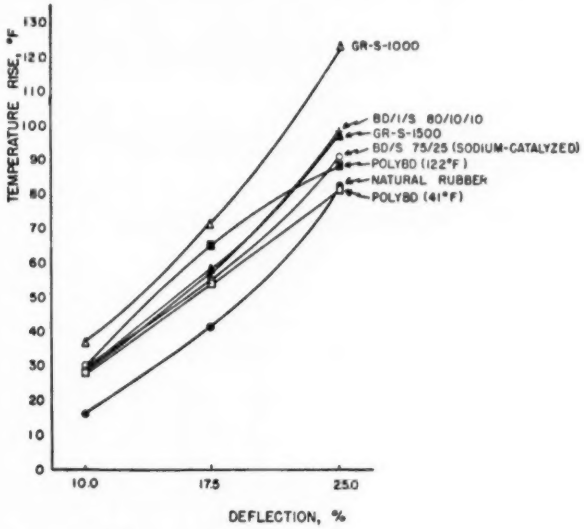


FIG. 6.—Effect of deflection on temperature rise (test temperature, 100° F).

TABLE 4

EFFECT OF VARYING DEFLECTION

(Load, 143 lb./sq. in.; test temperature, 100° F; frequency, 1800 r.p.m.)

	Min. cured at 292° F	Deflection (%) Shore-A hardness	Initial comp. (%)			30-min. temp. rise (° F)			Set (%)		
			10.0	17.5	25.0	10.0	17.5	25.0	10.0	17.5	25.0
Natural rubber*	25	53	26.9	25.3	25.4	27	57	145	2.5	11.8	34.5
	45	57	22.4	20.9	21.8	22	42	88	1.4	4.4	†24.9
	65	60	20.6	20.7	19.2	16	41	82	1.5	4.6	†23.9
GR-S-1000	65	62	21.0	20.5	22.7	42	82	139	2.0	8.0	19.7
	95	64	19.4	17.9	18.6	37	71	123	1.7	5.0	11.0
GR-S-1500	55	62	19.8	18.6	18.9	33	65	112	1.8	5.3	13.8
	85	64	16.6	16.2	17.7	29	58	97	1.1	2.4	7.4
Polybutadiene (122° F)	50	59	21.5	23.6	22.6	30	63	121	2.3	6.0	18.1
	80	60	20.5	21.6	22.7	30	65	88	1.3	4.5	11.6
(41° F)	50	65	15.4	15.1	15.1	29	60	‡62	1.4	2.7	4.2
	80	66	14.1	14.8	14.1	28	54	§81	0.8	2.8	1.0
BD/I/S/ 80/10/10	80	63	17.4	15.4	16.3	30	56	104	1.2	2.6	6.2
	100	63	16.8	15.4	16.3	29	57	≠98	1.4	2.3	3.9
BD/S 75/25 (Na-catalyzed)	55	59	23.8	24.6	24.9	34	69	112	2.8	8.2	20.0
	85	61	22.6	21.7	19.9	30	55	91	2.8	4.6	—

* Cured at 280° F.
† Test exceeded 30 minutes.
‡ Seven-minute test.
§ Eight-minute test.
≠ Twenty-minute test.

TABLE 5

EFFECT OF APPLIED LOAD

(Throw, 17.5%; test temp., 212° F.; frequency, 1800 f.p.m.)

	Min. cured at 292° F	Load (lb./sq. in.) Shore-A hardness	Initial comp. (%)			30-min. temp. rise (° F)			Set (%)		
			90	115	143	90	115	143	90	115	143
Natural rubber*	25	53	19.6	24.7	25.1	44	82	†63	38.9	44.8	‡42.4
	45	57	15.3	19.0	20.1	26	30	§39	15.3	‡32.6	‡37.0
	65	61	14.5	17.2	18.6	25	27	⁼33	11.3	†21.5	22.3
GR-S-1000	65	65	16.1	19.2	20.7	46	46	55	9.5	12.4	15.4
	95	65	15.4	18.1	18.8	41	41	46	6.2	8.4	8.8
GR-S-1500	55	63	13.3	16.7	19.0	37	36	45	7.9	10.3	14.2
	85	65	11.0	14.0	16.5	34	32	39	4.4	5.8	7.4
Polybutadiene (122° F)	50	60	15.2	18.1	21.0	37	37	48	10.0	12.8	16.5
	80	62	15.2	16.8	17.3	35	35	40	6.9	9.2	9.5
(41° F)	50	66	10.4	12.1	13.6	33	38	39	5.5	6.9	8.6
	80	67	0.92	12.4	15.1	29	34	37	3.3	4.6	6.7
BD/I/S 80/10/10	80	63	11.4	14.7	15.9	32	33	38	3.6	5.8	7.1
	100	63	11.0	14.5	16.1	34	31	38	3.5	5.2	5.1
BD/S 75/25 (Na-catalyzed)	55	61	19.1	21.7	25.0	31	35	40	12.9	15.7	19.3
	85	61	15.8	19.8	20.0	26	25	29	7.5	9.5	11.3

* Cured at 280° F.
† Tested 46 minutes, temperature rise 92° F.
‡ Test exceeded 30 minutes.
§ Tested 66 minutes, temperature rise 85° F.
⁼ Tested 80 minutes, temperature rise 77° F.

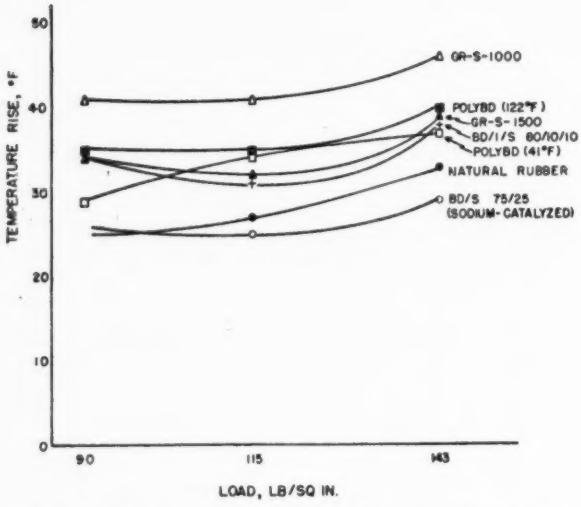


FIG. 7.—Effect of load on temperature rise (test temperature, 212° F).

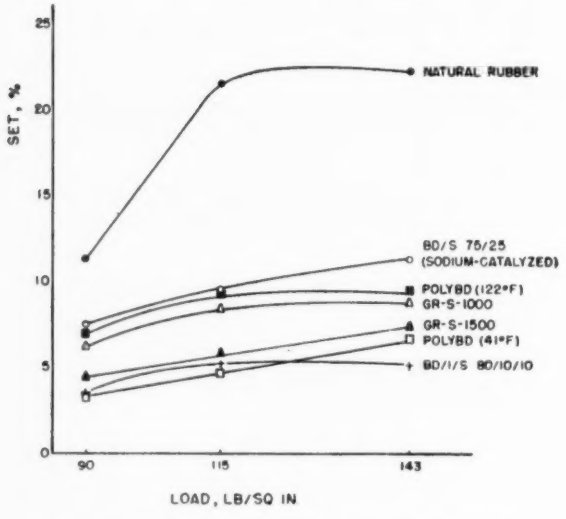


FIG. 8.—Effect of load on set values (test temperature, 212° F).

a difference of about 5° to 6° F. It is noted that, regardless of testing temperature, compounds mixed according to a tread type recipe should not be tested at a deflection of greater than 17.5 per cent because of the increase in slope beyond this deflection at 100° F.

The reputation of the Goodrich flexometer for reproducibility has undoubtedly been impaired by the failure to set the throw on the eccentric of the ma-

chine at the proper distance from the center to obtain a deflection of exactly 17.5 per cent. The vernier provided is not very accurate, and this adjustment should be made by means of a dial gauge calibrated to 0.001 inch. The gauge should be clamped to the upper frame with the foot of the gauge resting on the cross-bar supporting the upper anvil. Some of these details are explained in "ASTM Standards on Rubber Products".[3]

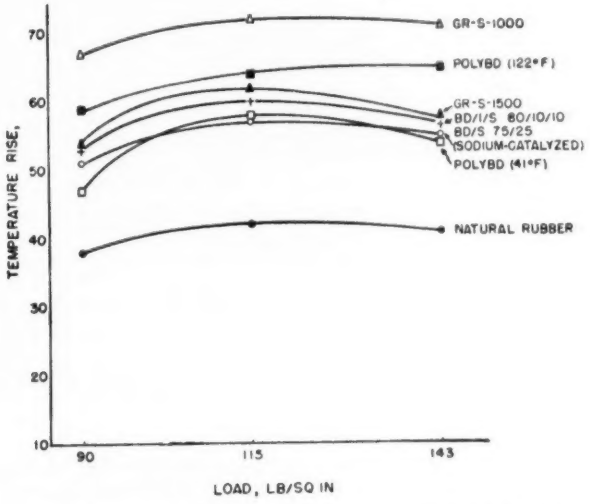


FIG. 9.—Effect of load on temperature rise (temperature, 100° F.)

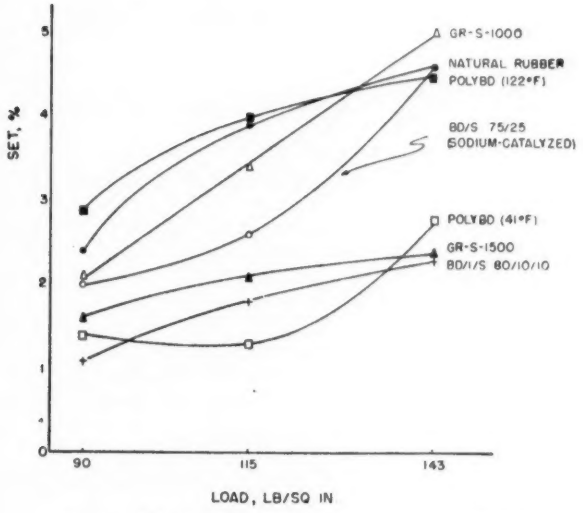


FIG. 10.—Effect of load on set values (temperature, 100° F).

TABLE 6

EFFECT OF APPLIED LOAD

(Throw, 17.5%; test temp., 100° F; frequency, 1800 f.p.m.)

	Min cured at 292° F	Load (lb./sq. in.)	Shore-A hardness	Initial comp. (%)			30-min. temp. rise (° F)			Set (%)		
				90	115	143	90	115	143	90	115	143
Natural rubber*	25		53	1.99	22.8	25.3	45	55	57	5.6	9.1	11.8
	45		56	14.9	18.1	20.9	39	42	42	2.7	3.1	4.4
	65		59	14.5	16.1	20.7	38	42	41	2.4	3.9	4.6
GR-S-1000	65		62	15.1	18.5	20.5	72	79	82	4.3	7.7	8.0
	95		64	12.9	17.6	17.9	67	72	71	2.1	3.4	5.0
GR-S-1500	55		61	13.9	16.7	18.6	64	67	65	3.0	3.6	5.3
	85		64	12.1	15.1	16.2	54	62	58	1.6	2.1	2.4
Polybutadiene (122° F)	50		59	16.0	18.6	23.6	59	64	63	3.2	5.2	6.0
	80		61	14.9	18.5	21.6	59	64	65	2.9	4.0	4.5
(41° F)	50		64	10.5	12.8	15.1	50	60	60	1.8	2.2	2.7
	80		65	9.7	12.9	14.8	47	58	54	1.4	1.3	2.8
BD/I/S 80/10/10	80		63	12.6	15.1	15.4	56	59	56	1.8	2.4	2.6
	100		63	11.8	14.7	15.4	53	60	57	1.1	1.8	2.3
BD/S 75/25 (Na-catalyzed)	55		58	15.9	20.4	24.6	51	63	69	3.6	5.7	8.2
	85		61	15.0	18.3	21.7	51	57	55	2.0	2.6	4.6

* Cured at 280° F.

EFFECT OF LOAD

The results obtained by varying the load are listed in Table 5, and the effects of load on temperature rise and set are shown in Figures 7 and 8. It is noted that a change in load has less effect on the temperature rise than any other test condition tried (*i.e.*, temperature, frequency or throw), and again an increase in state of cure has caused less effect on results with respect to the variations in test conditions. It appears from these data that an error of 5 lb./sq. in. load would not make more than 1° F difference of temperature rise at the cure levels shown. In view of the calibration, wherein the balance bar is leveled and a known actual weight is applied, it is not logical to assume that an error greater than 5 lb./sq. in. would be made.

The variation in set values with a change of load is also very small, except for the compound of natural rubber, as shown in Figure 8.

Varying the applied load at a temperature of 100° F causes an anomaly not apparent from the tests at 212° F (Table 6, Figures 9 and 10). Six of the seven compounds had higher hysteresis-temperature rise with a 115 lb./sq. in. load than with a 143 lb./sq. in. load. A difference of 4° to 5° F of temperature rise over the entire load range of 90 to 143 lb./sq. in. was observed for compounds of GR-S-1000, 122° F polybutadiene, and natural rubber. With the other polymer compounds, the increase of the rise with an increase in load of from 90 to 115 lb./sq. in. was 6° to 11° F, but, in every case, the rise decreased between 115 to 143 lb./sq. in.

The set values increase slightly as the applied load is increased.

CONCLUSIONS

The relation between the testing temperature (100, 158, and 212° F) and the hysteresis-temperature rise of the synthetic polymers at the cures used was found to behave as a linear function. The slopes of the lines seem to indicate that the relative order of efficiency of the vulcanizates varies at different temperatures of test and cure levels.

Frequency variations at 212° F ranged from 980 to 1800 flexures per minute. The temperature rise is a linear function of the frequency for all compounds tested. The increase of temperature rise with an increased rate of flexing is approximately uniform for all compounds (about 2° F per 100 f.p.m.) at the cure levels studied. The state of cure is shown to influence the rate of change of the temperature rise with the change in frequency.

The relation of the degree of deflection to the temperature rise characteristics of the rubber samples at 100 and 212° F was studied at 10, 17.5 and 25. per cent deflections. An error of deflection of one percentage unit will cause a 3° to 4° F error in the 10-minute temperature rise value. As the state of cure or the temperature decreases, the error in the temperature rise increases.

A change of load has less effect on the temperature rise and set values than any of the other conditions investigated.

Most of the lack of reproducibility among laboratories is probably due to failure to adjust precisely the throw (deflection of the specimen) of the test apparatus which is being used.

REFERENCES

[1] Lessig, *Ind. Eng. Chem. Anal. Ed.* **29**, 582 (1937); RUBBER CHEM. & TECHNOL. **11**, 249 (1948).
[2] Mackay, Anderson, and Gardner, *Trans. Inst. Rubber Ind.* **16**, 123 (1940); RUBBER CHEM. & TECHNOL. **14**, 421, 938 (1941).
[3] American Society for Testing Materials, "ASTM Standards on Rubber Products", Dec. 1952 edition, p. 334.

COLORIMETRIC DETERMINATION OF 2-MERCAPTO-BENZOTHIAZOLE IN COMPOUNDED RUBBER *

B. B. Bauminger and F. C. J. Poulton

Chemical Research Division, Research Center, Dunlop Rubber Co. Ltd., Fort Dunlop, Erdington, Birmingham, England

INTRODUCTION

With the extensive employment of organic accelerators in rubber technology, a corresponding demand has grown for analytical methods to determine both their identity and quantity, sometimes in compounded unvulcanized rubber, but more frequently in the finished vulcanized product. This need is reflected in the considerable volume of published work devoted to this branch of rubber analysis, but only a small fraction of this literature is concerned with the quantitative aspect. Methods involving the reaction of the organic accelerator with a metal ion have generally found most favor, no doubt because in many cases colored complexes are formed, which are often specific for a given accelerator. In the case of MBT, for example, the following reactions take place in benzene solution:

Cobalt	Green coloration[1]
Nickel	Reddish-brown coloration[2]
Copper	Orange precipitate[1]
Lead	Pale yellow precipitate[3]
Cadmium	White precipitate[4]
Bismuth	Yellow coloration[5]

With the exception of cobalt, these reactions seem reasonably specific for MBT, at any rate with respect to other common accelerators.

Quantitative methods for MBT have, in the main, been based on the formation of a benzene-insoluble precipitate. The copper oleate method of Wistinghausen[1] in particular has found a wide measure of acceptance, although Mogoricheva and Korsunskaya[6] claim that a volumetric finish to Wistinghausen's original procedure gives greater accuracy. A disadvantage of both procedures, however, is that inconveniently large quantities of sample are often required in order to obtain a working quantity of the accelerator. In some cases the necessary sample amounts to 20–30 grams, and this feature immediately places a severe restriction on possible applications of the method. In view of this limitation little work appears to have been carried out to eliminate the second defect of the Wistinghausen method, namely, the tendency to give low recovery of MBT from all but the simplest unvulcanized rubber compounds.

The amount of residual MBT which can be finally recovered from a rubber compound often differs markedly from that originally added. Many factors contribute to this discrepancy; some, such as those arising from adsorption of the accelerator on the carbon black, are associated with distinctive characteristics of the rubber compound under examination, while others can be con-

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 2, pages 100–113, April 1953.

trolled, or even eliminated, by adopting a suitable analytical procedure. An adequate study of interfering factors was undertaken as a major part of this investigation; they can be summarized into the following groups:

(1) Factors associated with chemical changes in the accelerator and its extraction from the rubber compound.
(2) Influence of other accelerators, antioxidants, and softeners.
(3) Losses introduced by accelerator adsorption on carbon blacks of various kinds.

Kress[7] has reported a spectrophotometric method for the determination of MBT, which he applied mainly to the determination of larger proportions of accelerator, such as occur in masterbatches. Such a method should be suitable for accelerator determination in normal vulcanized and unvulcanized stocks, but spectrometric methods as yet cannot be adopted in the majority of control testing laboratories. It was to meet the requirements of such laboratories that the method presented in this paper was developed. It is sufficiently sensitive to require only normal macroquantities of sample, *i.e.*, 1–2 grams, is reasonably quick and specific, and demands only the conventional type of absorptiometer for the final color measurement.

EXPERIMENTAL

First experiments, based on the formation of the nickel complex, were directed to the establishment of optimum conditions necessary for the full development of the reddish-brown color of the nickel salt. Nickel oleate was selected as the most suitable reagent, since the complex with MBT is soluble in benzene over a fairly wide range of concentration, and also because nickel exhibits a reasonable degree of specificity towards MBT.

With recrystallized MBT in benzene solution, a linear relationship was shown to exist between concentration of MBT and the optical density, using an Ilford 601 filter in conjunction with a Spekker absorptiometer. The solution was heated with a benzene solution of nickel oleate at 75° C, and the maximum color developed in 30 minutes. It was verified that no measurable fading took place within 1 hour.

Attention was then turned to the determination of MBT extracted from rubber. A simple pale crepe mixing containing 1 per cent of the recrystallized accelerator was extracted with acetone for 16 hours. The extract, after drying, was dissolved in benzene, and treated at 75° C with a calculated excess of nickel oleate reagent, and the optical density of the resulting solution measured on the Spekker absorptiometer at room temperature.

The results were very low and suggested considerable loss of MBT, either from failure to extract the accelerator from the mixing by means of acetone, or by volatilization of the MBT by incautiously heating the dried extract. Determination of sulfur in the extract, however, revealed the theoretical amount, and it was concluded that the formation of the colored nickel-MBT complex was being inhibited by an extractable component of the rubber.

It does not fall within the scope of the present paper to discuss the precise nature of the agent responsible for suppressing the formation of the reddish-brown nickel complex, but further work in connection with the phenomenon has confirmed this experience. For instance, a known amount of MBT, on being refluxed with the nonrubber material extracted with acetone from pale crepe, gave a response on treatment with nickel oleate which was only about 30

per cent of that expected. On the other hand, when the same amount of MBT was milled into rubber which had previously been extracted with acetone, its recovery and estimation by the nickel oleate procedure was only slightly less than theoretical. Clearly therefore, direct treatment of the extract with nickel oleate is not a suitable basis for an analytical method for the estimation of MBT.

A more promising approach was to treat the acetone extract from the rubber with dilute ammonium hydroxide, thereby separating the MBT from most of the other ingredients of the extract. Reaction with nickel ion was then carried out in the aqueous phase, using a mixture of nickel and ammonium chlorides. The colored nickel complex thus formed was extracted with benzene for absorptiometric measurement.

Other workers[8] have remarked on the tendency of MBT to oxidize to the disulfide during milling and vulcanizing. Similar conversion was also noted during the course of this investigation. The extent of the oxidation was found to vary with processing conditions and was particularly evident in vulcanizates. Determination of the free MBT in such compounds will, therefore, give only a partial account of the amount of accelerator originally present, since the disulfide does not react with the nickel reagent. In order to determine the total MBT, the disulfide must be reduced to the original form. Throughout the present paper these two forms have been designated free residual MBT and total MBT, respectively, and it was presumably failure to recognize this distinction that formed a major cause of the low results obtained by Wistinghausen's method.

The procedure finally adopted for the determination of MBT was as follows:

To the acetone extract from 2 grams of the rubber sample, carefully dried at room temperature, add 10 cc. hot sodium sulfide solution (20 per cent w/v) and boil gently. Filter when cold and acidify the filtrate with 2*N* hydrochloric acid. Boil gently to remove hydrogen sulfide, and remove the liberated MBT by benzene extraction. Reduce the volume of the benzene solution if necessary by careful evaporation, transfer to a 25-cc. standard volumetric flask and adjust to volume.

Pipette a 10-cc. aliquot of this solution into each of two small beakers and evaporate to dryness at room temperature. Dissolve each in 10 cc. of warm ammonium hydroxide (0.5 *N*) and transfer to two separating funnels, one of which contains 15 cc. nickel chloride reagent (prepared by mixing equal volumes of 6 per cent nickel chloride w/v and 3 per cent ammonium chloride w/v), and the other, acting as a control, 15 cc. ammonium chloride solution (2 per cent w/v). Rinse each beaker with 5 cc. of the appropriate aqueous reagent and add to the funnel. Shake to form the nickel complex.

Extract both solutions with 10-cc. portions of benzene, evaporate to 20 cc., and transfer to 25-cc. standard volumetric flasks. After adjusting to volume at 20° C, measure the optical density of the solutions and determine the MBT content of the test solution by reference to a calibration curve prepared by measuring the optical density of MBT solutions prepared from the purified material.

For the determination of free residual MBT it is unnecessary to carry out a reduction with sodium sulfide, and the dried acetone extract can be treated immediately with warm ammonium hydroxide. Aliquots of the filtered solution are then treated with nickel chloride reagent, and the estimation continued as before described.

The calibration curves obtained on a Spekker absorptiometer are shown in Figure 1. Each calibration point is the mean of four determinations, and the fact that individual deviations from the means ranged only between −0.04 and +0.02 for a total of sixteen determinations gives a measure of the precision of the benzene extraction and the measuring techniques. Curve A shows the relationship between the drum reading of the instrument (*i.e.*, optical density of the solution) and quantities of MBT up to 15 mg., using a 0.5-cm. cell and Ilford-601 filter. With quantities of less than 5 mg., it becomes necessary to recalibrate with a larger cell (2 cm.), and this relationship is shown in Curve B.

First experiments on the recovery of MBT from compounded rubber were conducted on a mixing of recrystallized MBT in pale crepe, adjusting the ac-

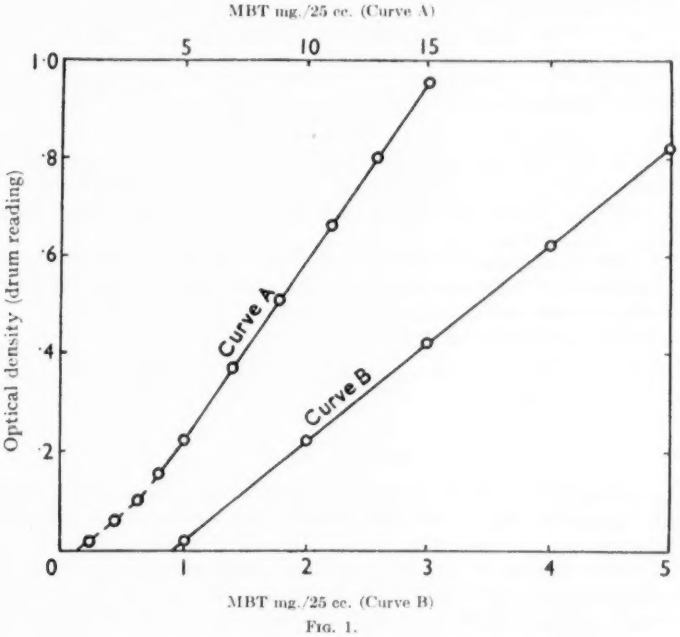


FIG. 1.

celerator content to 1 per cent. Both total and free residual MBT were determined by the methods already described, with corresponding control samples from the original rubber being treated similarly. Mix A in the Table below was prepared without cooling water passing through the rolls, thus permitting the mixing temperature to rise to approximately 60° C, while the temperature of B was restricted to about 35° C during mixing by the use of cooling water. The results are shown in Table 1.

It will be seen that there is substantial agreement between the total MBT recovered and the theoretical amount present; this confirms that nonrubber components are not interfering and that extraction for sixteen hours with hot acetone is adequate for complete removal of the accelerator from the rubber. In the past, doubt has often been expressed as to whether sixteen hours is sufficient for complete extraction of MBT from vulcanized mixings, and low

results by Wistinghausen's method have sometimes been ascribed to this cause. It is evident from the above results that, whatever degree of decomposition occurs as an accompaniment of mixing and vulcanizing, all unchanged MBT will appear in the acetone extract within sixteen hours, and the failure of sub-subsequent analysis to obtain more complete recovery lies probably in faulty quantitative methods.

With regard to free MBT, in mix B the figure is virtually coincident with that for the total, and this may be taken as an indication that no measurable

TABLE 1

RECOVERY OF MBT FROM PALE CREPE/MBT MIXING

	Present (per cent)	Found (per cent)	
		Free	Total
Mix A	1.0	0.93	0.98
		0.94	0.98
Mix B	1.03	1.03	1.02
		1.02	

oxidation to MBTS takes place as the accelerator is extracted from the rubber with hot acetone. The somewhat lower figures obtained in mix A are consistent with a small amount of oxidation to MBTS which was presumably induced by the higher mixing temperature[9].

The effect of normal milling and vulcanizing procedure, such as obtains in the preparation of compounded rubbers, on the ultimate recovery of MBT was studied in a simple rubber compound of the following composition which was mixed in a period of ten minutes.

Pale crepe (masticated)	100
Sulfur	3
MBT	0.75
Stearic acid	3
Zinc oxide	5

The commercial MBT used in this compound yielded, on assay, a figure of 96.5 per cent; allowing for this, the mixed stock had a pure MBT content of 0.65 per cent.

Two-gram portions of the compound were extracted with hot acetone for 16 hours, and the extracts treated as before to determine both free residual and total MBT. The results from nine successive pairs of determinations are collected in Table 2.

TABLE 2

RECOVERY OF MBT FROM COMPOUNDED UNVULCANIZED RUBBER

	Free MBT (per cent)	Total MBT (per cent)
1st day	0.48	0.58
	0.46	0.60
2nd day	0.47	0.57
	0.48	0.58
3rd day	0.47	0.60
	0.46	0.56
4th day	0.48	0.60
	0.48	0.56
5th day	0.46	0.58
Mean	0.47	0.58
Range	0.02	0.04

The reproducibility of the results with regard to both free MBT and total MBT is within ±5 per cent, and can be regarded as reasonably satisfactory for a determination of this type. The mean recovery of total MBT is just under 90 per cent, and indicates a loss greater than that sustained in the simple pale crepe-accelerator mixing.

Since the previous work had shown that extraction with acetone of the accelerator from the rubber was complete and that the assay of MBT in the extract was substantially quantitative, the loss of free accelerator is evidently associated with the incorporation of the compounding ingredients. Oxidation to MBTS induced by the mixing process, *i.e.*, that due directly to atmospheric oxidation seems to play only a minor part, since not only did thorough mixing of the accelerator and rubber in the pale-crepe mixing (Table 1) fail to reduce to an appreciable extent the free MBT recovery, but the compounded rubber (Table 2) on further milling gave results only very slightly lower.

TABLE 3

RECOVERY OF MBT FROM REMILLED UNVULCANIZED COMPOUNDED RUBBER

	Free MBT (per cent)	Total MBT (per cent)
1st day	0.44	0.60
2nd day	0.46	0.60
3rd day	0.44	0.59

This was shown by taking three samples of the unvulcanized compound to which Table 2 relates and milling them with a roll temperature of 80° C for a further 10 minutes (*i.e.*, extending the previous milling time by an equal amount), and carrying out MBT determinations as before. Only three estimations were made, the object being to reveal any major trend away from results in Table 2 rather than to assess the significance of slight differences. Figures for remilled material are given in Table 3.

VULCANIZED COMPOUNDS

For the study of the recovery of MBT from vulcanized rubbers, the same compound was used, and specimens were cured at 138° C for 10, 25, 50, and 100 minutes, to pass well beyond the point of optimum cure.

The results are presented in Table 4.

The recovery of both total and free MBT shows a steady decline, until after 100 minutes only about a half of the MBT added to the rubber compound

TABLE 4

RECOVERY OF MBT FROM VULCANIZED RUBBER

Cure at 138° C (min.)	Free MBT (per cent)	Total MBT (per cent)
10	0.43	0.60
	0.44	0.61
25	0.41	0.58
	0.40	0.58
	0.40	0.58
50	0.38	0.57
	0.38	0.55
		0.54
100	0.34	0.53
	0.31	0.51
		0.51

appears in the original form. Some 30 per cent of the accelerator oxidizes to MBTS under these conditions, and when this is reconverted to MBT, the recovery is improved to approximately 80 per cent. At the point of optimum cure, about thirty minutes at the temperature selected, just over 60 per cent of the MBT originally added is in the free form, while a further 25 per cent has oxidized to MBTS.

Perhaps the most interesting feature, however, of the comparison between unvulcanized and vulcanized rubber is the relatively greater oxidative breakdown or fixation of the MBT at the milling stage compared with its changes during vulcanization. This, no doubt, is due in part to its oxidation to MBTS which, in such cases, appears to be catalyzed by zinc oxide. Moreover, the general assumption seems to have been that although the disulfide is formed as an intermediate stage in the vulcanization of MBT stocks, such combination takes place in the early stages of heating; the possibility of the reaction taking place at lower temperatures seems not to have been considered.

Summarizing the accelerator changes which take place in the course of processing the rubber stock, it appears that during the first ten minutes of mixing almost 30 per cent of the MBT is oxidized to MBTS, but this rapid rate of transformation is not maintained, since an additional ten minutes' mixing produces only a further 3 per cent drop in the free MBT content. This would suggest that an equilibrium is reached to which a number of factors, such as milling conditions, relative proportions of zinc oxide and accelerator, contribute. Vulcanization causes no measurable increase in the oxidation rate, which follows a steady linear relationship with time.

The total MBT content follows a similar course, but the initial loss after twenty minutes' mixing is very much less, amounting to only 10 per cent of the original MBT. During vulcanization, the total MBT content also declines at a fairly uniform rate, the result of this being that the MBTS content remains at a remarkably constant figure of about 0.2 per cent throughout vulcanization.

Further work will be undertaken to study the fate of MBT in mixing and vulcanizing and to follow the significant roles of zinc oxide and stearic acid in this connection.

INTERFERENCE FROM ANTIOXIDANTS

Some antioxidants form colored complexes with certain metal salts. To investigate possible interference with the quantitative recovery of MBT, four widely used antioxidants were examined for their influence on the recovery of MBT from unvulcanized and vulcanized stocks. The effect of these antioxidants on the formation of the disulfide was also investigated.

A wider range of antioxidants was examined qualitatively for their reactivity towards nickel ion. In these cases the antioxidants were not extracted from rubber mixings, but were treated directly with ammonium hydroxide or sodium sulfide, according to whether their influence on the free MBT or total MBT figure was being assessed. Nickel chloride reagent was then added as before, and the aqueous solution extracted with benzene. As the amount of antioxidant used for the tests was many times that normally extracted from a compounded rubber, visual comparison of the respective benzene extracts for the presence of colored complexes would have provided adequate evidence of interference. Commercial forms of the following antioxidants were thus treated, all gave a completely negative response to the procedure for both free and total MBT:

Condensation product of di-*o*-cresylolpropane with dimethylamine and formaldehyde.
Mixtures of bis-(2-hydroxy-3,5-dimethylphenyl)alkylmethanes (probable composition of Nonox-EX).
2,2′-Methylene bis-(4-methyl-6-*tert.*-butylphenol).
2,6-Di-*tert.*-4-methylphenol.
Condensation product of di-*o*-cresylolpropane with piperidine and formaldehyde.
p-Phenylphenol.

Dialkylphenol sulfide gave no coloration after the procedure for free MBT, but after treatment with alkali sulfide, a benzene-soluble compound was formed which produced a faint yellow coloration. The color was so feeble, however, that its effect on the quantitative estimation of MBT would be quite undetectable.

The effect of the following four commercial antioxidants on the recovery of MBT was studied quantitatively:

Condensation product of α- and β-naphthylamines with acetaldehyde.
Polymerized trimethyldihydroquinoline.
Phenyl-β-naphthylamine.
sym-Di-β-naphthyl-*p*-phenylenediamine.

The stock had the following composition:

Pale crepe	100
Sulfur	3.4
Stearic acid	2.3
Zinc oxide	5.7

After mixing, the batch was divided equally, and MBT in mother-stock form added to one of the portions so that the concentration of accelerator was 1.18 per cent. Five aliquots were then taken from each of the two portions and into four of these was mixed 0.5 per cent of the appropriate antioxidant. There were thus five corresponding pairs of samples—four pairs with antioxidant, with and without accelerator, and a pair of controls both without antioxidant, with and without accelerator.

The series containing accelerator was then divided into two portions, one of which was vulcanized (30 minutes at 138° C), thus making a total of fifteen samples.

Acetone extracts from the fifteen specimens were prepared in duplicate, one extract from each pair being reserved for the determination of free MBT, and the other being treated first with aqueous sodium sulfide in order to determine the extent of any conversion of the accelerator to disulfide.

The effect of the four antioxidants on the recovery of MBT from unvulcanized and vulcanized stocks is shown in Table 5.

The amount of total MBT determined in the unvulcanized stock is reasonably constant and is equivalent to a mean recovery of approximately 90 per cent; hence 0.5 per cent of the antioxidants examined is without measurable effect on the decomposition of MBT. In the estimation of free MBT, however, the figures are consistently higher than the control to a degree that excludes the possibility of experimental error, and it is tentatively concluded that the antioxidant reduces the tendency of the original MBT to form the disulfide.

TABLE 5

EFFECT OF FOUR ANTIOXIDANTS ON RECOVERY OF MBT

Antioxidant	Unvulcanized stocks		Vulcanized stocks	
	Free MBT (per cent)	Total MBT (per cent)	Free MBT (per cent)	Total MBT (per cent)
Condensation product of α- and β-naphthylamines and acetaldehyde	0.70	1.04	0.59	0.87
Polymerized trimethyldihydroquinoline	0.69	1.03	0.47	0.93
Phenyl-β-naphthylamine	0.66	1.07	0.55	1.02
Sym-di-β-naphthyl-*p*-phenylenediamine	0.63	1.06	0.43	0.99
Control (no antioxidant)	0.55	1.03	0.47	0.86

Results on the vulcanized compounds for both free and total MBT are more erratic, and provide no clear evidence that antioxidant influences the formation of either MBTS or further breakdown products.

INTERFERENCE FROM OTHER ACCELERATORS

The sensitivity of the nickel chloride reagent towards other common accelerators was investigated by applying the procedure already outlined to a series of laboratory prepared mixings based on the following stock:

Pale crepe	100
Sulfur	3
Stearic acid	3
Zinc oxide	5

The following accelerators were then milled into aliquots of the stock: zinc diethyldithiocarbamate 0.5, tetramethylthiuram disulfide 0.7, mixture of diphenylguanidine and dinitrophenylbenzothiazolyl sulfide 1.0, diphenylguanidine 0.7, N-cyclohexyl-2-benzothiazyl sulfenamide 1.0.

Each sample was divided into two portions, one of which was vulcanized at 138° C for 25 minutes, the other remaining unvulcanized.

In both unvulcanized and vulcanized compounds the majority of the accelerators tested failed to give a measurable color for total MBT, when tested with nickel chloride reagent. Mixtures of diphenylguanidine and dinitrophenyl benzothiazolyl sulfide, and N-cyclohexyl-2-benzothiazyl sulfenamide both gave fairly strongly colored benzene solutions—a result that would be expected from the breakdown products of these accelerators.

INTERFERENCE FROM PINE TAR AND SIMILAR SOFTENERS

Besides antioxidants, other benzene-soluble ingredients of the acetone extract may interefere, either by virtue of their own color or by the formation of a colored nickel compound. Softeners, particularly dark-colored materials such as pine tar and coal tar products, are likely sources of error of this type, and were, in fact, found to give benzene solutions many times more intense in color than is likely to be met in any normal MBT determination.

The initial treatment of the acetone extract with dilute ammonium hydroxide does not in such cases, effect a clear-cut extraction of the hydrophilic components, since the ammonium fatty acid soaps effectively emulsify the tarry matter. In this form the tar resists the simpler techniques of separation,

and is subsequently taken into the benzene layer after the normal procedure with nickel chloride reagent has been carried out.

When the total MBT is being determined, however, treatment with aqueous sodium sulfide precedes the separation of accelerator from the rest of the extract, and it has been found that this separation is not accompanied by emulsification of the nonaqueous matter. Tarry materials, therefore, will not interfere with the determination of the total MBT.

In the determination of free MBT, saturated sodium carbonate solution was found to dissolve the accelerator without emulsifying the tar, and separation of the alkaline salt is achieved by passing through a filter paper, wetted with sodium carbonate solution. After acidifying the filtrate with dilute hydrochloric acid, the liberated MBT is extracted with warm benzene, evaporated very carefully to dryness, and treated with aqueous ammonia, nickel chloride reagent, and benzene in the usual manner.

ADSORPTION BY CARBON BLACK

Although much work has been done on the assessment of carbon blacks by measuring their adsorptive capacities towards organic accelerators, no values for the adsorption of accelerator within a rubber mixing have been reported. This problem is important to the compounder and is of converse interest to the analyst, to whom it appears as a source of major error in the determination of MBT in a vulcanized product. It was to throw some light on the latter aspect that the following experiments were carried out.

The MBT-MBTS equilibrium, which has been shown in earlier investigations to be of considerable importance, was, in this case, not of primary interest, and emphasis for this series of determinations lay, therefore, in estimating the recovery of total MBT.

The stock had the following composition:

Smoked sheet	100
Sulfur	3.5
Stearic acid	3.5
Zinc oxide	5.2

Into aliquots of this, the following rubber carbons were mixed at a concentration of 49 per cent, calculated on the rubber; Micronex Beads, lampblack, Philblack-O, Wyex. MBT accelerator was then added to each of the black stocks to bring the accelerator content to 0.49 per cent, and the samples were subdivided to enable recoveries from vulcanized and unvulcanized rubbers to be compared.

Results are collected in Table 6.

TABLE 6

RECOVERY OF MBT FROM BLACK STOCKS

Type of black	Unvulcanized total MBT (per cent)	Vulcanized total MBT (per cent)
Micronex	0.20	0.11
Lampblack	0.42	0.29
Philblack-O	0.26	0.15
Wyex	0.28	0.16
Control (no black)	0.44	0.30

Possibly the most important feature revealed by these results is the surprisingly low recoveries of accelerator from the unvulcanized stocks. The control sample showed an MBT content in accordance with previous work (90 per cent of theoretical), and the amount determined in the lampblack compound (0.42 per cent) was virtually the same. From the two channel and furnace black compounds, however, only about half the added quantity was extracted, and presumably this represents the proportion available for acceleration.

In vulcanized stocks, the recovery of accelerator is even further reduced, and demonstrates that, even after reconversion of MBTS to MBT, the determination of MBT by any method which involves a preliminary extraction of accelerator with a solvent is likely to produce results which bear little resemblance to the original figure. Although only four blacks were examined in the foregoing tests, they were sufficiently representative of types in common use to show the wide variation in the degree of accelerator adsorption that takes place within the rubber mixing. Since this variation must also be affected by the relative proportion of black to accelerator, and to a lesser extent, probably, by processing and vulcanizing, it would be difficult to form a reliable estimate of the interference in any particular case, particularly where the nature of the black is unknown. Further experience might show that a rough classification of adsorption effects based on types of black would be feasible.

In the above tests on unvulcanized and vulcanized black stocks, certain other factors which tend to reduce the apparent MBT content have been eliminated by treatment with sodium sulfide; had free residual MBT been determined the figure would have been considerably lower.

DISCUSSION AND CONCLUSION

The direct reaction between MBT and a benzene soluble nickel salt, for example, nickel oleate, to give a red-brown compound, is not a satisfactory basis for the quantitative determination of MBT in compounded rubber, since certain nonrubber ingredients of raw rubber inhibit the development of the color. Theoretical results can be obtained, however, by treating the MBT in the acetone extract from the rubber first with dilute ammonia and then with aqueous nickel chloride reagent; the nickel-MBT complex thus formed is dissolved in benzene.

A variety of other factors, bearing on the recovery of the original amount of MBT from the rubber, has been studied at some length, but as rubber stocks vary so enormously in composition, and in their response to mixing and vulcanizing conditions, there is little point in attempting to make a general assessment of such interferences. A division of these factors, very roughly according to magnitude, is however, as follows:

ADSORPTION ON CARBON BLACK

As would be expected, the adsorption of MBT on channel black is most marked, and in some unvulcanized compounds less than half the MBT originally added is extractable with acetone. As vulcanization proceeds, the amount recoverable is even less, amounting in some cases to only a quarter of the original. These recovery figures, particularly from the unvulcanized material, reflect to some extent the amount of MBT available for acceleration, and from the analytical standpoint indicate the considerable error that is introduced by failing to take adsorption effects into account.

OXIDATION OF MBT TO MBTS

Depending on processing conditions, a substantial proportion of the original MBT is oxidized to MBTS, and investigations into this aspect of MBT estimation fully support the views of Dufraisse and Houpillart[10] that an equilibrium between MBT and its disulfide is set up during vulcanization. It appears that this equilibrium condition is established comparatively soon after processing has commenced, and a feature of continued vulcanization is the constancy of the MBTS content. For analytical purposes, a preliminary reducing treatment is available so that the disulfide can be reconverted to MBT and included in the final determination.

Following the addition of zinc oxide to a rubber mixing, the free MBT content shows a sharp drop suggesting that the zinc oxide catalyzes the oxidation of the accelerator to MBTS. Treatment with alkaline sulfide again restores the original MBT.

OXIDATION OF MBT TO IRRECOVERABLE TRANSFORMATION PRODUCTS

This factor is largely responsible for the relatively small but persistent loss that prevents 100 per cent recovery of the MBT from most compounded rubbers, and since it depends on processing and curing conditions, it is of more significance in vulcanized than unvulcanized stocks.

INTERFERENCE FROM OTHER COMPOUNDING INGREDIENTS

With increasing complexity of the mixing, there seems to be a tendency for the oxidation of MBT to follow a less predictable course. A wide range of antioxidants and other accelerators are examined, and there was no evidence of systematic interference with the main reaction with nickel ion, although recoveries on the whole were slightly more erratic. Where antioxidants form strongly colored benzene solutions, their effect can be counteracted by measuring the adsorption, in the same wave band, of a benzene solution of the acetone extract taken as a control.

Dark-colored softeners such as pine tar which would cause a similar interference can be eliminated by extracting the accelerator from the bulk of the acetone extract with sodium carbonate or sulfide.

SUMMARY

A method for the determination of 2-mercaptobenzothizaole (MBT) in compounded rubber is based on the formation and evaluation of the red-brown color obtained by reacting the alkaline salt with nickel ion.

Application of the method to a variety of compounded rubbers has shown that MBT can be determined with a reasonable degree of certainty in only the simplest rubber mixings. In general, the more complex in composition and the more processing the mixing has undergone, the further will the figure for MBT recovery deviate from the amount originally incorporated.

The effect of the other compounding ingredients, notably antioxidants, other accelerators, and softeners, from which considerable interference was anticipated, is in fact negligibly small. Among common accelerators the reagent can be regarded as specific, but the decomposition of those accelerators which yield MBT will naturally be reflected in the final results.

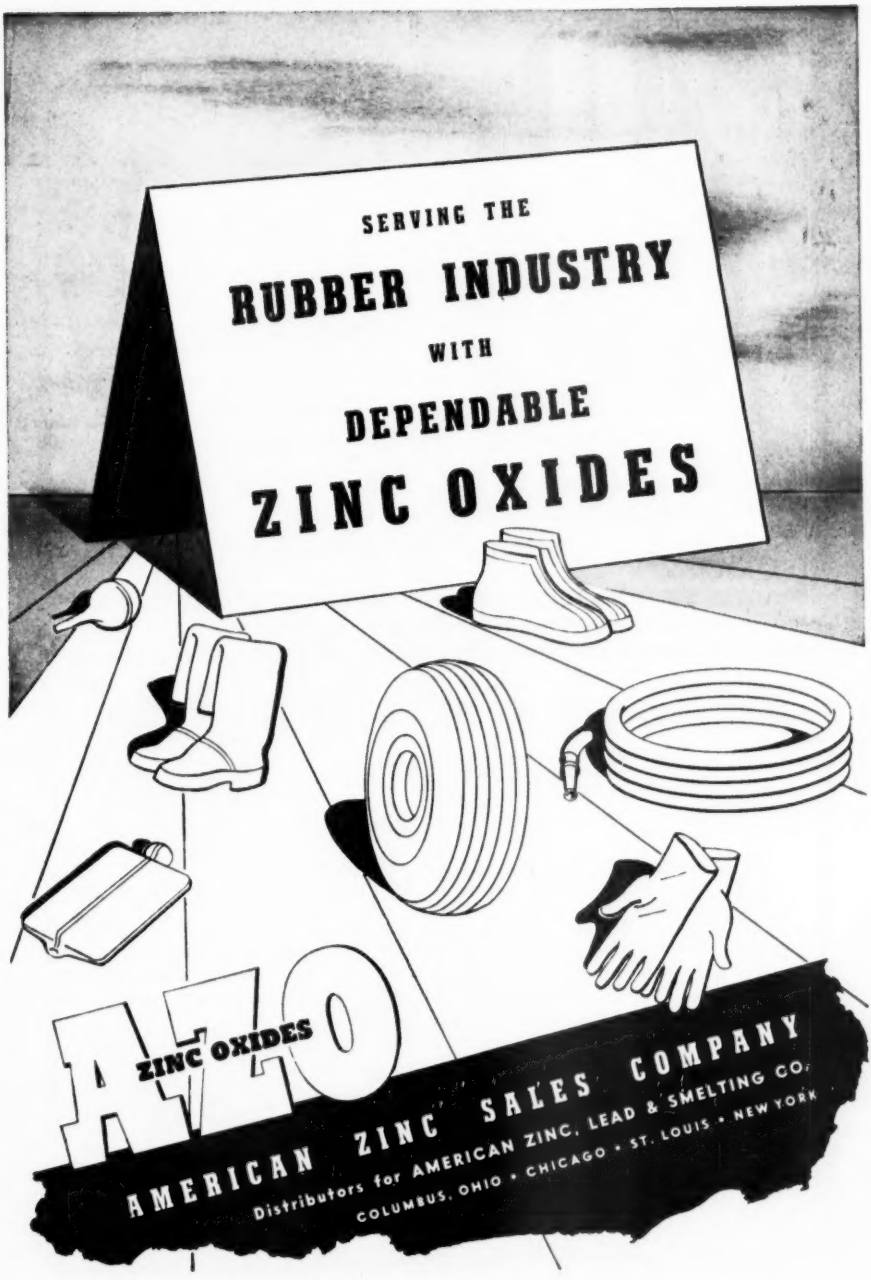
High mixing temperatures and longer vulcanizing times favor the transformation of MBT to the disulfide (which, however, can be estimated by reconversion to MBT), and to simpler breakdown products.

ACKNOWLEDGMENT

The authors wish to thank the Dunlop Rubber Co. Ltd. for permission to publish this work. They would also like to acknowledge the help of P. F. Lloyd in the experimental work on adsorption of MBT in carbon black stocks.

REFERENCES

[1] Von Wistinghausen, *Kautschuk* **5**, 77 (1929).
[2] Shimada, *J. Soc. Rubber Ind. Japan* **10**, 339 (1937).
[3] Spacu and Kuras, *Bull. soc. sci. Cluj* (Roumania) **8**, 243 (1935).
[4] Spacu and Kuras, *J. prakt. Chem.* **144**, 106 (1935).
[5] Schaefer, *Kautschuk and Gummi* **1**, 149 (1948).
[6] Mogoricheva and Korsunskaya, *J. Rubber Ind.* (USSR) **10**, 341 (1933).
[7] Kress, *Anal. Chem.* **23**, 313 (1951).
[8] Dufraisse and Houpillart, *Rev. gén. caoutchouc* **19**, 207 (1942); Montu, *Rev. gén. caoutchouc* **29**, 506 (1952).
[9] Twiss, *India-Rubber J.* **108**, 731 (1945).
[10] Dufraisse and Houpillart, *Rev. gén. caoutchouc* **19**, 207 (1942).


SERVING THE
RUBBER INDUSTRY
WITH
DEPENDABLE
ZINC OXIDES
AZO
ZINC OXIDES
AMERICAN ZINC SALES COMPANY
Distributors for AMERICAN ZINC, LEAD & SMELTING CO.
COLUMBUS, OHIO • CHICAGO • ST. LOUIS • NEW YORK

The C.P. Hall Co.
CHEMICAL MANUFACTURERS

ACCELERATORS
PLASTICIZERS
ANTIOXIDANTS

A Complete Line of Approved Compounding Materials

● AKRON, OHIO • LOS ANGELES, CALIF. • CHICAGO, ILL. • NEWARK, N. J.

STAMFORD "FACTICE" VULCANIZED OIL

(Reg. U. S. Pat. Off.)

Our products are engineered to fill every need in natural and synthetic rubber compounding wherever the use of vulcanized oil is indicated.

We point with pride to a complete line of solid Brown, White, "Neophax" and "Amberex" grades, and hydrocarbon solutions of "Factice" for use in their appropriate compounds.

Continuing research and development in our laboratory and rigid production control has made us the leader in this field.

The services of our laboratory are at your disposal in solving your compounding problems.

THE STAMFORD RUBBER SUPPLY COMPANY

STAMFORD, CONNECTICUT

Manufacturers of "Factice" Brand Vulcanized Oil
Since 1900

Now Available—

Second Edition of

LATEX in INDUSTRY

By ROYCE J. NOBLE, Ph.D.

912 Pages • 6 x 9 Inches • 25 Chapters
Bibliography • Author Index • Subject Index

PRICE: $15.00* Postpaid in U. S.
$16.00 Postpaid in All Other Countries

1953-54 Edition of

RUBBER RED BOOK

Directory of the Rubber Industry

Ninth Issue — 1200 Pages

Completely Revised and Up-to-Date

PRICE: $10.00* Postpaid in All Countries

(*) Add 3% Sales Tax for Copies to New York City Addresses

Published by

RUBBER AGE

250 West 57th St. New York 19, N. Y.

To the
Rubber Industry! ~ ~ ~

This Journal is supported by advertising from leading suppliers to the industry. More advertising will permit the publication of a greater number of important technical papers on rubber which will make RUBBER CHEMISTRY AND TECHNOLOGY even more valuable as a convenient reference of "Rubberana."

Specify materials from suppliers listed on page 30. Urge other suppliers to advertise in

RUBBER CHEMISTRY AND TECHNOLOGY

●

Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, c/o E. I. du Pont de Nemours & Company, 40 E. Buchtel Ave. at High Street, Akron 8, Ohio.

Ready Now!

MACHINERY and EQUIPMENT for RUBBER and PLASTICS

VOLUME I
PRIMARY MACHINERY AND EQUIPMENT

The only book of its kind ever offered to the Rubber and Plastics Industries and the first to be published since Pearson's "Rubber Machinery" in 1915. Compiled by Robert G. Seaman and Arthur M. Merrill, the present Editors of India RUBBER WORLD, with the cooperation of an Editorial Advisory Board of experts in their respective fields. Each chapter is preceded by an article written by recognized authorities on the equipment, its purposes for specific products, and best method of using it.

Volume I has over 800 pages of editorial content with authoritative descriptions for each machine classification: Types, Specifications, Design Features, Operation, and Applications, as well as names and addresses of the manufacturers or suppliers. More than 300 illustrations. Cloth-bound for permanence.

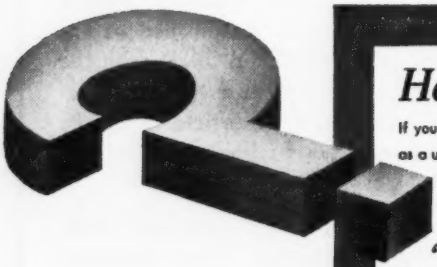
Send for free copy of complete prospectus.

Volume I—$15.00 Postpaid in U. S. A.
$16.00 Elsewhere

Volume II—Supplementary Machinery and Equipment, is now in preparation and will be published in the near future.

INDIA
RUBBER WORLD
386 FOURTH AVENUE NEW YORK 16, N. Y.

WHY St. Joe lead-free Zinc Oxide



Here is the Answer:

If you were to name the principal factors that you—as a user of zinc oxide—would consider all-important when choosing a supplier, wouldn't this be the line-up?

a. Integrity and experience of the manufacturer.

b. High quality and uniformity of the product.

c. The producer's ability to deliver, *on time*, the precise type of pigment and the quantities you need.

On those, *and many other counts*, the St. Joseph Lead Company stands out. As a result, ST. JOE American Process, Lead-Free ZINC OXIDES have for years been specified by many manufacturers who are known for the high quality of their own products.

ST. JOSEPH LEAD COMPANY
250 PARK AVENUE • NEW YORK 17 • ELdorado 5-3200
Plant & Laboratory, Monaca, (Josephtown), Pennsylvania

ANTIMONY SULPHIDE

Regular Grades *for* Attractive Color

Also

A special grade for obtaining colored stocks having high abrasion resistance

RARE METAL PRODUCTS CO. **ATGLEN, PENNA.**

SUPERIOR ZINC CORPORATION

121 North Broad Street **Philadelphia 7, Penna.**

Works at Bristol, Pa.

RUBBER SUBSTITUTES

(Vulcanized Vegetable Oils)

Manufactured since 1903 by

THE CARTER BELL MFG. CO.

SPRINGFIELD NEW JERSEY

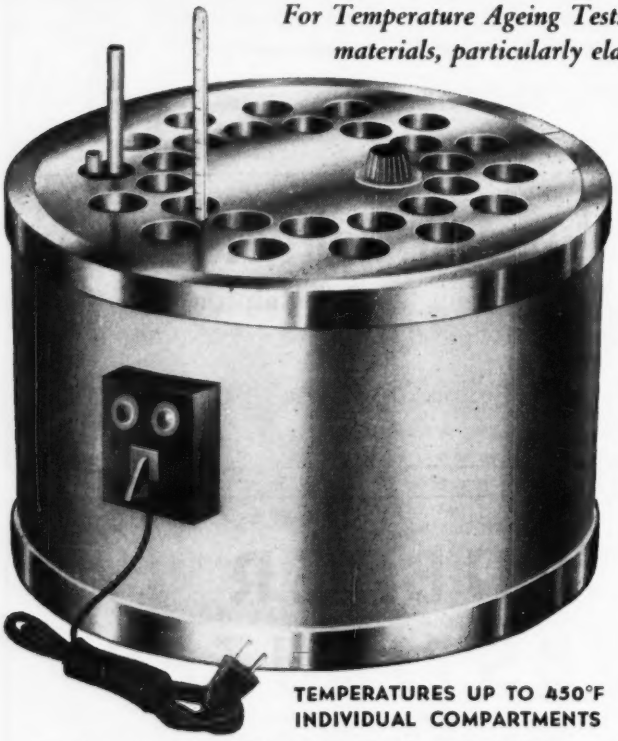
Represented by:

HARWICK STANDARD CHEMICAL CO.

Akron — Boston — Trenton — Chicago — Denver — Los Angeles

NEW Scott Aluminum Block Heating Bath

For Temperature Ageing Tests of organic materials, particularly elastomers



Also for OXYGEN AGEING STUDIES

TEMPERATURES UP TO 450°F
INDIVIDUAL COMPARTMENTS

Here is an insulated solid aluminum block oven, developed originally for oxygen absorption studies, now produced as a standard Scott Tester* model available also for oven ageing studies of rubber, silicones and other elastomeric materials. With built-in electric heating elements and temperature controls it eliminates the hazards of heating with immersion oils and is also much cleaner, while the individual isolated compartments eliminate errors due to contamination between samples. Made in 2 standard arrangements: 28 compartments approximately 1½" dia. for temperature ageing; also with a lesser number of larger compartments for oxygen ageing. Can also be furnished in other compartment arrangements if your particular needs require it.

*Registered Trademark

Request Literature

SCOTT TESTERS, INC. 102 Blackstone St. Providence, R. I.

Scott Testers — Standard of the World

WHITETEX

A new white and bright pigment for rubber, synthetic rubber or plastics, especially vinyls.

BUCA

A proved pigment for compounding ALL types of natural and synthetic rubber.

CATALPO

For compounding rubber and synthetic rubber.

No. 33 CLAY

For wire and vinyl compounding.

●

For full details, write our Technical Service Dept.

SOUTHERN CLAYS, INC.

(Formerly P. W. Martin Gordon Clays, Inc.)

33 Rector Street · New York 6, N.Y.

CARBON BLACKS

Wyex (EPC)
Easy Processing Channel Black

Arrow TX (MPC)
Medium Processing Channel Black

Essex (SRF)
Semi-Reinforcing Furnace Black

Modulex (HMF)
High Modulus Furnace Black

Aromex (HAF)
High Abrasion Furnace Black

Aromex 115 (CF)
Conductive Furnace Black

Aromex 125 (SAF)
Super Abrasion Furnace Black

Arovel (FEF)
Fast Extruding Furnace Black

Collocarb
80% Carbon Black + 20% Process Oil

CLAYS

Suprex Clay . . . . High Reinforcement
Paragon Clay . . . . . Easy Processing
Hi-White R . . . . . White Color

RUBBER CHEMICALS

Turgum S, Natac, Butac . . . . . Resin-Acid Softeners
Aktone . . . . . Accelerator Activator
Zeolex 20 . . . . . Reinforcing White Pigment

HUBER J. M. HUBER CORPORATION • 100 Park Ave., New York 17, New York

consult **TITANOX** *technical service department*

for assistance with your white pigmentation problems

1660

TITANIUM PIGMENT CORPORATION

Subsidiary of NATIONAL LEAD COMPANY

TITANOX
the brightest name in pigments

THE VANDERBILT MODEL LABORATORY

NORWALK, CONNECTICUT

Here we learn how our materials can be used by our customers to their best advantage. We invite and appreciate your cooperation.

Please feel free to visit our laboratory, to discuss your problems with us and to use our facilities to work them out if you care to do so.

R. T. VANDERBILT CO., Inc.

230 Park Avenue, New York City

RUBBER CHEMISTRY AND TECHNOLOGY IS SUPPORTED BY ADVERTISING FROM THESE LEADING SUPPLIERS

INDEX TO ADVERTISERS

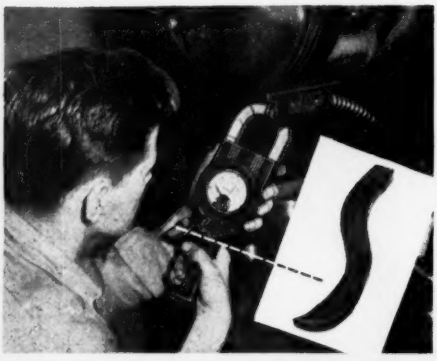
	Page
American Cyanamid Company, Calco Chemical Division	11
American Zinc Sales Company	19
Binney & Smith Company...(Opposite Table of Contents)	18
Cabot, Godfrey L., Inc.	9
Carter Bell Manufacturing Company, The	25
Du Pont Rubber Chemicals Division	10
General Atlas Carbon Company	31
Goodrich, B. F., Chemical Company	32
Goodyear Tire & Rubber Company, The	5
Hall, C. P. Company, The	20
Harwick Standard Chemical Company (Inside Back Cover)	
Huber, J. M., Corporation	28
India Rubber World	23
Koppers Company, Inc. (Chemical Division)	15
Monsanto Chemical Company	6
Naugatuck Chemical Division (U. S. Rubber Company)	12
Neville Company, The	13
New Jersey Zinc Company, The (Outside Back Cover)	
Pan-American Refining Corp., Pan American Chemicals Div.	8
Phillips Chemical Company (Opposite Inside Front Cover)	1
Rare Metal Products Company	25
Richardson, Sid Carbon Company	7
Rubber Age, The	21
St. Joseph Lead Company	24
Scott Testers, Inc	26
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	27
Stamford Rubber Supply Company, The	20
Sun Oil Company, Sun Petroleum Products (Opposite Title Page)	16
Superior Zinc Corporation	25
Thiokol Corporation, The	4
Titanium Pigment Corporation	28
United Carbon Company (Inside Front Cover)	
Vanderbilt, R. T. Company	29
Witco Chemical Company	2

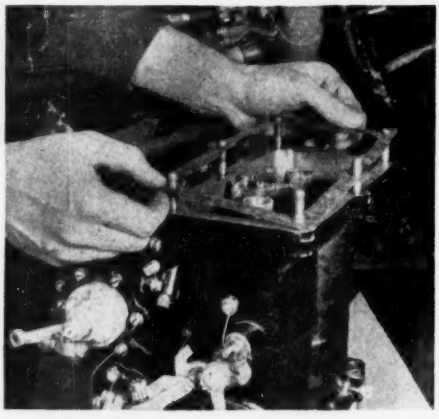
for
the
best...
CABOT
SRF
CARBON
BLACK
PELLETEX
®
General Atlas Division
of Cabot Carbon Company
GODFREY L. CABOT, INC.
77 FRANKLIN STREET
BOSTON 10, MASS.

More developments using

B. F. Goodrich Chemical *raw materials*

B. F. Goodrich Chemical Company does not make these products. We supply the Hycar rubber only.





ON AIRCRAFT, OIL WELL AND ELECTRICAL JOBS

. . . versatile Hycar scores high!

LOOK at the three typical uses of Hycar pictured. They show the wide range of applications for this versatile American rubber. And they also show how Hycar helps improve products and operations—save money.

The carburetor gasket is used on a Navy helicopter. Hycar bonds the asbestos fibers of the gasket, helps seal power *in*—keep trouble *out*. Hycar resists heat, oil, solvents and retains its high tensile strength. It helps make the gasket non-absorbing, non-swelling and non-cracking.

The Hycar rubber "O" ring seal is one of many uses for Hycar in the petroleum industry. It's used on a powerful pump designed for jet bit, big hole and deep drilling. The Hycar "O" ring seals tightly, resists abrasion and the hydrocarbons entrained in the drilling fluid.

On the volt-ammeter, the trigger is made with a Hycar rubber-phenolic compound. Breakage under sudden pressure which used to plague rag-filled phenolic triggers has been reduced almost to zero.

Hycar's many advantages may be the perfect answer to your product improvement or development problems—and your sales plans. We'll help you select a Hycar rubber compound exactly suited to your needs. For technical information, please write Dept. HD-4, B. F. Goodrich Chemical Company, Rose Building, Cleveland 15, Ohio. Cable address: Goodchemco. In Canada: Kitchener, Ontario.

B. F. Goodrich Chemical Company
A Division of The B. F. Goodrich Company

Hycar
American Rubber

GEON polyvinyl materials • HYCAR American rubber • GOOD-RITE chemicals and plasticizers • HARMON colors

Material for ALL RUBBER and PLASTIC COMPOUNDING

COLORS

FILLERS

SOFTENERS

EXTENDERS

PLASTICIZERS

RESINS . . .

PARA-COUMARON INDENES
HYDRO-CARBON TERPENES
MODIFIED STYRENES
AROMATIC HYDRO-CARBONS

PRECISION Uniformity

You can depend upon the *Precision* character of Harwick Standard Chemicals regardless of the quantity requirement . . . Here is dependable assurance of uniformity in any type compounding material for rubber and plastics to give *certainty* in product development and production runs.

Our services are offered in co-operative research toward the application of any compounding material in our line to your production problems.

HARWICK STANDARD CHEMICAL CO.

AKRON 5, OHIO

BRANCHES: BOSTON, TRENTON, CHICAGO, LOS ANGELES

You can formulate *FASTER... BETTER* with

HORSE HEAD® ZINC OXIDES

FORMULATE *FASTER!*

...Because the Horse Head line comprises the most complete family of Zinc Oxides for rubber:

1. It is the only line having such a wide range of particle sizes, surface conditions and chemical compositions.
2. Its *conventional* types cover the range of American and French Process oxides.
3. Its *exclusive* types include the well-known Kadox and Protox brands.

That means you need not waste time adapting a single Zinc Oxide to each specific compound. Instead, just choose from the Horse Head line the Zinc Oxides that best meet your needs.

FORMULATE *BETTER!*

...Because you need to compromise less when you choose from the wide variety of Horse Head Zinc Oxides.

...Because the Horse Head brands can improve the properties of your compounds.

Year after year, for nearly a century, more rubber manufacturers have used more tons of Horse Head Zinc Oxides than of any other brands.

THE NEW JERSEY ZINC COMPANY

Founded 1848

160 Front Street, New York 7, N. Y.